

# Thermal diffusivity measurements in a lyotropic discotic nematic phase

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Received 17 March 2007; received in revised form 16 May 2007; accepted 16 May 2007

Available online 24 May 2007

Communicated by V.M. Agranovich

## Abstract

The present work is focused on thermal diffusivity ( $D$ ) measurements, via  $Z$ -scan experiment, in a discotic nematic phase of the lyotropic mixture comprised of potassium laurate, decanol and  $D_2O$ . In this experiment, the nematic sample is translated through the focal region of a focused Gaussian laser beam. The experimental data are analyzed according to the thermal lens model and the ratio between the thermal diffusivities parallel ( $D_{\parallel}$ ) and perpendicular ( $D_{\perp}$ ) to the director of the nematic sample has been found to be smaller than one. The results are compared to others obtained with different liquid crystals and explained by using a simple model where this ratio is correlated to the shape anisotropy of the micelles.

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PACS: 61.30.-v; 64.70.Md; 42.65.Jx

## 1. Introduction

One important branch of research with liquid crystals rises when a laser beam passes through these materials. The absorbed energy is converted into heat and several nonlinear phenomena can be induced as a result of this interaction. Discrimination among these nonlinear phenomena has been achieved by changing the beam power and polarization and the experimental configuration [1,2]. In this context, was introduced the  $Z$ -scan technique and conceived as being a simple and efficient method to measure the nonlinear optical response of a medium material [3]. At milliseconds (ms) time range, the nonlinear optical response is expected to be of thermal and orientational origin [1,2]. This nonlinear study has been employed particularly in thermotropic materials but there are few data concerning the lyotropic liquid crystals (LLC) [4]. These systems are formed by mixtures of amphiphilic molecules and a solvent (usually water), under convenient temperature and concentration condi-

tions. The basic units of the LLC are anisotropic micelles [5]. From the classical phase diagram reported by Yu and Saupe [6], two uniaxial nematics and one biaxial nematic phases were characterized. The uniaxial nematic lyotropic phases are known as prolate (calamitic  $N_C$ ) and oblate (discotic  $N_D$ ) micellar aggregates dispersed in water [5]. These phases presents negative (positive) optical and positive (negative) diamagnetic anisotropies, respectively. In this phase diagram the conventional isotropic phase ( $I$ ) is observed at high temperature as well as one reentrant isotropic phase ( $I_{RE}$ ) which takes place at lower temperatures. The biaxial nematic phase ( $N_B$ ) appears, in this phase diagram, as an intermediate phase between the uniaxial nematic phases. These nematic lyotropic phases have been recently investigated, from a linear optical point of view, by means of the refractometry technique [7–9].

In this Letter, through the use  $Z$ -scan technique, we report on measurements of the thermal diffusivity ( $D$ ) in a discotic nematic phase at room temperature ( $T = 25^\circ\text{C}$ ) in a lyotropic mixture of potassium laurate, decanol and  $D_2O$ . It is well known in liquid crystal materials that the thermal diffusivity is an anisotropic parameter [10,11]. In this sense, this study requires the measurements of two thermal diffusivities,  $D_{\parallel}$  and

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$D_{\perp}$ , 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. Our experimental results are analyzed according to the thermal lens model (TLM) as described by Palffy-Muhoray et al. [13] and the ratio  $D_{\parallel}/D_{\perp}$  has been found to be smaller than one. On the other hand, has been reported in the literature that this ratio is greater than one in all the liquid crystal samples investigated [11,14]. From theoretical point of view, these results indicate that the thermal anisotropy in thermotropic liquid crystals can be related to the molecular dimensions [10]. In this way, our experimental results are discussed by using a simple model that correlates the  $D_{\parallel}/D_{\perp}$  to the shape anisotropy of the micelles [12,14].

## 2. Fundamentals

The Z-scan is an efficient and powerful nonlinear optical technique [3]. It was developed to measure nonlinear optical parameters of a material and it presents high sensitivity when compared to conventional interferometry. In Z-scan 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. 1. Our experimental setup includes a diode laser Ventus MPC600 (from Quantum) with power output adjusted to 47 mW. The beam waist radius  $\omega_0$  is about  $21.5 \mu\text{m}$  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 values of the thermal diffusivity for a thermal nonlinear optical response can be determined from fitting the spatial dependence on  $z$  and the temporal dependence via thermal lens model [13,15]. The normalized light transmittance ( $\Gamma$ ), as a function of  $z$  and time  $t$ , can be written as [13]:

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

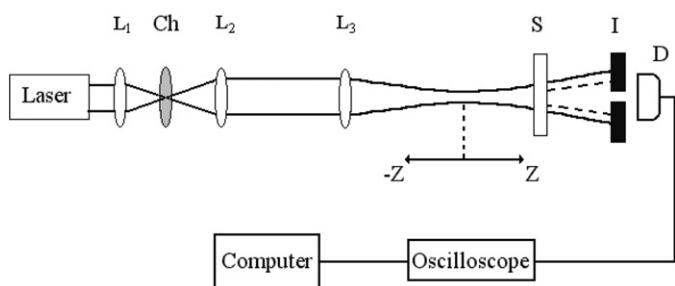


Fig. 1. Sketch of the Z-scan apparatus.  $L_1$ ,  $L_2$ , and  $L_3$  are lenses; Chopper (Ch); Sample (S); Iris (I) and Detector (D).

where  $x = z/z_0$ ,  $z_0$  is the confocal parameter,  $\theta = 2.303 (-dn/dT)\alpha P/\lambda k$  is the phase shift [16] (phase difference between the center and the outer edge of the beam),  $t_{co} = \omega_0^2/4D$  is the characteristic thermal time,  $D = k/\rho C_P$  is the thermal diffusivity,  $P$  is the power of the laser beam,  $\lambda$  is the wavelength of the laser,  $\alpha$  is the linear optical absorption,  $dn/dT$  is the thermo-optical coefficient,  $k$  is the thermal conductivity,  $\rho$  is the density and  $C_P$  is the specific heat. Eq. (1) is valid under the condition that  $\theta \ll 1$  [13]. In liquid crystal medium,  $\theta$ ,  $t_{co}$  and  $D$  are anisotropic parameters. These parameters,  $\theta_{\parallel}(\theta_{\perp})$ ,  $t_{co\parallel}(t_{co\perp})$  and  $D_{\parallel}(D_{\perp})$ , are defined in a direction parallel (perpendicular) to the director of the nematic sample.

The lyotropic mixture investigated in this work [6,18] was prepared with the following concentrations in weight percentage: potassium laurate (KL: 24.80), 1-decanol (DeOH: 6.24) and  $D_2O$  (68.96). DeOH (> 99% purity) and  $D_2O$  (> 99% purity) are commercially available from Aldrich. KL was synthesized in our laboratory from lauric acid via neutralization with potassium hydroxide and was further recrystallized with ethanol several times; the compounds for this synthesis came from Merck. The phase sequences, as determined by optical microscopy, digital image processing [17] and refractive index measurements [8], are as follows: reentrant isotropic  $I_{RE}$  ( $12.1^\circ\text{C}$ ) discotic nematic  $N_D$  ( $36.3^\circ\text{C}$ ) isotropic  $I$ . The nematic sample was conditioned in sealed planar glass cells (1 mm of light path) from Hellma. Uniform orientation of the sample was performed using an electromagnet ( $H = 10 \text{ kG}$ ) 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  $x$ - $y$  plane of the sample is defined with  $x$ ( $y$ ) axis parallel to the length (width) of the cells. The homeotropic alignment of the sample is produced by a magnetic field of 10 kG parallel to the  $x$ -axis of the laboratory frame combined with rotations of the sample around the  $z$ -axis. A small quantity of ferrofluid (< 0.04 wt.%) was added to the discotic nematic sample in order to ensure a good quality alignment of the director in the  $N_D$  phase. The measurements were

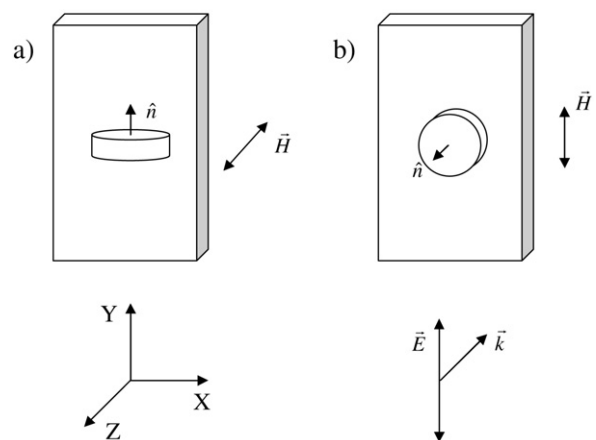


Fig. 2. Experimental configuration of the nematic director, magnetic field and the laser beam polarization for thermal diffusivity measurements of (a)  $D_{\parallel}$  and (b)  $D_{\perp}$  on the  $N_D$  phase.

made at  $T = 25^\circ\text{C}$  in a controlled temperature device stable at 10 mK. The anisotropic parameters  $\theta$ ,  $t_{co}$  and  $D$ , can be obtained by orientation of the director  $\hat{n}$  along two perpendicular directions, so the configurations between  $\hat{n}$  and the laser beam polarization  $\vec{E}$  are  $\hat{n} \parallel \vec{E}$  and  $\hat{n} \perp \vec{E}$ , respectively. Fig. 2 shows

a scheme of the relative configuration of the nematic director, magnetic field and polarization of incident laser beam for measurements of these parameters in the  $N_D$  phase.

### 3. Results and discussion

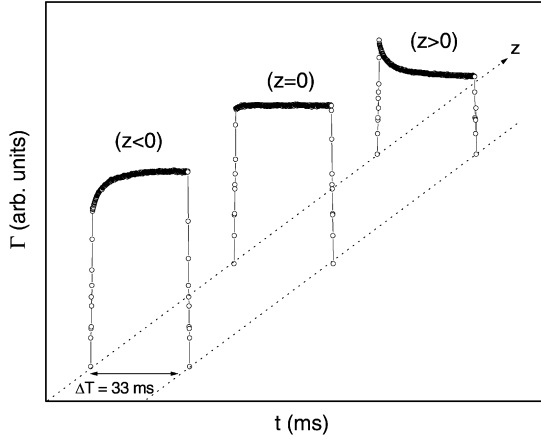


Fig. 3. Time evolution of the optical transmittance in three successive positions of the nematic sample along the  $z$  axis.

Fig. 3 presents typical time evolution curves of the optical transmittance in three positions of the nematic sample along  $z$ -axis. Fig. 4(a) shows a typical Z-scan curve obtained for the discotic nematic phase at temperature  $T = 25.0^\circ\text{C}$ . The experimental data are obtained according to Eq. (1) by means of a self-consistent fitting of  $\theta$  and  $t_{co}$  parameters. The fitting procedure employed here is the same utilized by Palfy-Muhoray et al. [13]. Fig. 4(b) shows typical time dependence transmittance at a fixed  $z$  position and the fit from Eq. (1). The experimental curves exhibited in Figs. 4(a) and 4(b) correspond to the  $N_D$  phase, for a laser beam traveling in the nematic medium with polarization parallel to the optic axis of the nematic sample. In the same way, similar curves were obtained in a perpendicular direction to the optic axis of the nematic phase (Figs. 4(c) and 4(d)). Taking the experimental values,  $\omega_o = 21.5 \mu\text{m}$  and  $t_{co} = \omega_o^2/4D$ , with  $t_{co\parallel}(t_{co\perp})$  anisotropic

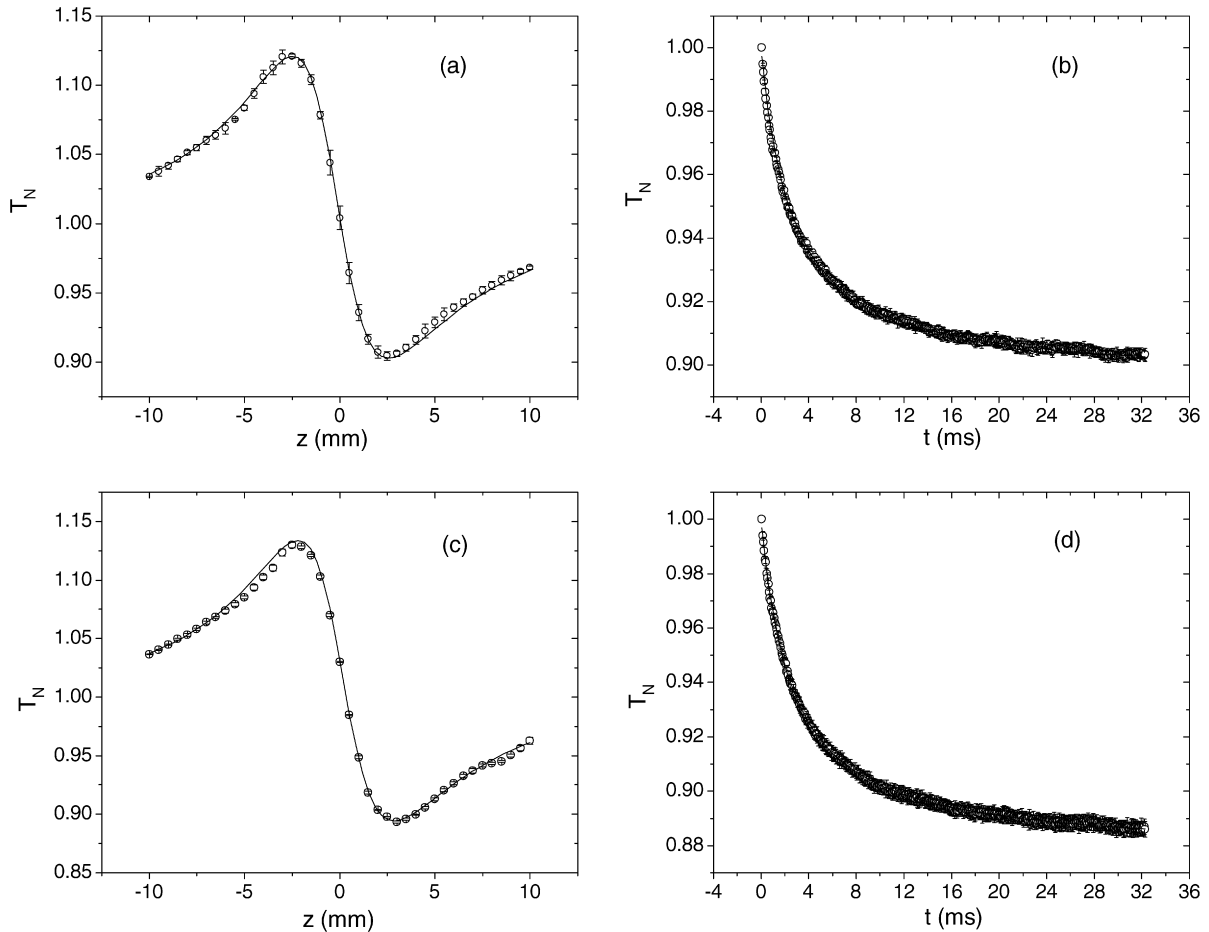


Fig. 4. Typical curves of Z-scan measurements on the lyotropic mixture ( $N_D$  phase), where (a) and (b) concerned to the configuration  $\hat{n} \parallel \vec{E}$  and (c) and (d) concerned to the configuration  $\hat{n} \perp \vec{E}$ . The solid lines (a) and (c) correspond to the fitting of Eq. (1) with  $t \sim 10 t_{co}$  for  $\theta_{\parallel} = 1.182 \times 10^{-3}$  and  $\theta_{\perp} = 1.294 \times 10^{-3}$ , respectively [13]. Typical time dependence transmittance (b) and (d) at fixed ( $z = 2.5 \text{ mm}$ ) position [16] and  $\theta_{\parallel}$  ( $\theta_{\perp}$ ) phase shift. The solid lines correspond to the fitting of Eq. (1) with  $\theta_{\parallel}(\theta_{\perp}) = 1.182(1.294) \times 10^{-3}$  for  $t_{co\parallel}(t_{co\perp}) = 2.62(2.43) \text{ ms}$  [13].

Table 1

Values of the characteristic thermal times, thermal diffusivities and ratio of the thermal diffusivities in the discotic nematic sample at  $T = 25^\circ\text{C}$ 

Phase	$t_{c\parallel}$ (ms)	$t_{c\perp}$ (ms)	$D_{\parallel}$ ( $10^{-8}$ ) $\text{m}^2/\text{s}$	$D_{\perp}$ ( $10^{-8}$ ) $\text{m}^2/\text{s}$	$D_{\parallel}/D_{\perp}$ (measured)	$D_{\parallel}/D_{\perp}$ (estimated)
$N_D$	$2.62 \pm 0.05$	$2.43 \pm 0.05$	$4.40 \pm 0.08$	$4.74 \pm 0.08$	0.93	0.88

parameters, into account, we obtain the parallel ( $D_{\parallel}$ ) and perpendicular ( $D_{\perp}$ ) thermal diffusivities defined, respectively, in a direction parallel or perpendicular to the director of the nematic sample, and the ratio  $D_{\parallel}/D_{\perp}$ . These important parameters are given in Table 1.

As can be seen in Table 1, the ratio  $D_{\parallel}/D_{\perp}$  is smaller than 1 in this discotic nematic phase. To our knowledge, there are no independent measurements of this ratio with this discotic nematic phase in the literature. However, some time ago the thermal diffusivity in a LLC was studied in a calamitic nematic phase [14] and it was proposed, as a first approach, that this phenomenon could be understood through a relation given by

$$\frac{D_{\parallel}}{D_{\perp}} = \frac{\frac{L_{\parallel}}{L_{\perp}}(1 + 2S) + (2 - 2S)}{\frac{L_{\parallel}}{L_{\perp}}(1 - S) + (2 + S)}. \quad (2)$$

The parameters  $L_{\parallel}$  and  $L_{\perp}$  defined in Eq. (2) are, respectively, the molecular dimensions parallel and perpendicular to the director direction and  $S$  is the scalar order parameter. An amazing aspect of this expression is that it predicts that if a calamitic nematic phase is replaced by a discotic one, the ratio  $D_{\parallel}/D_{\perp}$  would change from a number greater than 1 to a number smaller than 1. This simple theoretical prediction is consistent with the experimental results determined in this work. Taking the ratio between the parameters  $L_{\parallel}/L_{\perp} \cong 0.76$  into account, obtained in this  $N_D$  phase via experiment of X-ray diffraction [19], and using  $S \cong 0.5$  [20] we obtain, from Eq. (2),  $D_{\parallel}/D_{\perp} \sim 0.88$ . This theoretical prediction, despite some limitations, is consistent with our experimental data as indicated in Table 1. It is important to mention that the symmetry of the micelles and their average distances were not taken into account in the theoretical approach of Eq. (2). Likewise, the fact that the micelles 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 must be also further considered. One possible way to overcome these difficulties could be the use of the Hess approach [21,22], which was originally conceived to study the viscosity of the nematic liquid crystals. This approach, which considers that the geometry generated by the interacting potential is the essence of the anisotropic behavior found on the liquid crystals phenomenology, has successfully described many theological problems and does not suffer from the limitations presented above.

To sum up, we have carried out a thermal diffusivity study in discotic nematic phase of deuterated lyotropic mixtures (KL/DeOH/D<sub>2</sub>O). To the best of our knowledge, this experiment presents a first investigation of this parameter, particularly in the discotic nematic phase. The experimental ratio

$D_{\parallel}/D_{\perp} < 1$  obtained for  $N_D$  phase is discussed in terms of a simple theoretical approach consistent with the nature of shape anisotropy of micellar aggregates characteristic of the lyotropic discotic nematic phase. The repeatability of our data, under the described experimental conditions, was checked and verified by this result. In this way, we have also determined this ratio for a calamitic nematic phase and the obtained result is the same as the one existing in the literature [14].

### Acknowledgements

We are thankful to the Brazilian Agencies CAPES, CNPq and Fundação Araucária (PR) for the financial support of this work.

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