PHYSICAL REVIEW E, VOLUME 64, 012701

Temperature dependence of the refractive index near the reentrant-isotropic−calamitic-nematic phase transition

J. R. D. Pereira,[1,2] A. M. Mansanares,[1]* A. J. Palangana,[2] and M. L. Baesso[2]
[1]*Instituto de Física Gleb Wataghin, Universidade Estadual de Campinas, Unicamp, Caixa Postal 6165,*
13083-970, Campinas, São Paulo, Brazil
[2]*Departamento de Física, Universidade Estadual de Maringá, Avenida Colombo, 5790, 87020-900 Maringá, Paraná, Brazil*

(Received 10 November 2000; published 6 June 2001)

The laser-induced nonlinear optical response of a lyotropic liquid crystal system in the reentrant-isotropic and calamitic-nematic phases is investigated by the use of the thermal lens technique. The occurrence of an inversion in the temperature coefficient of the ordinary refractive index, $dn_\perp/dT$, near the reentrant-isotropic–calamitic-nematic phase transition, is discussed. This effect is attributed to the behavior of the electronic polarizability due to the change in micelle shape near the isotropic-nematic transition, and correlated with the results obtained near the nematic-isotropic transition, previously reported.

DOI: 10.1103/PhysRevE.64.012701 PACS number(s): 61.30.−v, 64.70.Md, 42.65.Jx

I. INTRODUCTION

One of the most fundamental aspects of research on liquid crystal systems is the determination of the macroscopic order parameters [1]. From the Landau–de Gennes theory it is possible to show that for lyotropic liquid crystal systems the order parameter $Q_{\alpha\beta}$ is directly related to the optical susceptibility [2]. In this sense, the optical birefringence $\Delta n = n_e - n_o$ is an important parameter for analyzing phase transitions in lyotropic liquid crystals, where n_e is the extraordinary and n_o is the ordinary refractive index. These systems are formed by mixtures of amphiphilic molecules and a solvent (usually water), under convenient temperature and concentration conditions. The basic units are anisotropic micelles [3,4]. Several methods of measuring Δn have been employed, particularly in thermotropic systems [5,6]. However, very few investigations have been reported on refractive indices or optical birefringence [7,8] associated with the nematic-isotropic phase transition in lyotropic liquid crystals. Another experimental method, the *Z*-scan technique, was used to measure the amplitude and sign of the nonlinear refractive index of a lyotropic mixture at room temperature [9]. In recent years, the thermal lens (TL) technique has been employed in the determination of both optical and thermal parameters of lyotropic liquid crystals [10–12], and recently it was used in the evaluation of the change of the refractive index near the calamitic-nematic–isotropic ($N_C \rightarrow I$) phase transition [12].

In this paper, we report the temperature dependence of the rate of change of the nonlinear ordinary and extraordinary refractive indices near the reentrant-isotropic–calamitic-nematic phase transition ($I_{\mathrm{re}} \rightarrow N_C$), obtained through thermal lens measurements. The occurrence of $dn_\perp/dT$ inversion near the reentrant-isotropic–nematic phase transition is discussed. This effect is attributed to the behavior of the electronic polarizability due to the change in micelle shape near the $I_{\mathrm{re}} \rightarrow N_C$ transition, and correlated with results obtained near the $N_C \rightarrow I$ transition, as previously reported [12].

II. EXPERIMENT

The lyotropic liquid crystal sample was prepared with the following composition: potassium laurate (29.1 wt %), decanol (6.4 wt %), and water (64.5 wt %) [13]. The phase sequences were determined by optical microscopy and conoscopic observations, which showed that it was isotropic up to 15 °C, calamitic nematic from 15.0 to 47.2 °C, and isotropic again above 47.2 °C. The width of the nematic-isotropic phase transition of this sample is approximately 1 °C. The sample was placed in a quartz cuvette with thickness $L = 0.5$ mm. The uniform alignment of the director is produced by a 0.8 T magnetic field parallel (planar) or perpendicular (homeotropic) to the sidewalls. To ensure the good quality of the alignment of the director, the magnetic field action was reinforced by adding a small quantity of ferrofluid (<0.05 wt %) to the nematic mixture. The sample temperature was controlled by a circulating temperature bath (Haake K-20/DC-5). The resolution of this temperature controller is 0.01 °C. For each orientation of the director, the measurements were performed as a function of the temperature in the range from 12 up to 52 °C, so that $dn_\parallel/dT$ and $dn_\perp/dT$ could be determined. 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 [14,15]. The details of the experimental setup are given in Refs. [10] and [12].

III. THEORY

A. Thermal lens

The thermal lens effect is created when an excitation laser beam passes through the sample and the absorbed energy is converted into heat, changing the refractive index and producing therefore a lenslike optical element within the sample. The propagation of the probe beam laser through the TL results in either a defocusing ($dn/dT < 0$) or a focusing ($dn/dT > 0$) of the beam center. The theoretical treatment of

---

*Electronic address: manoel@ifi.unicamp.br

the TL effect takes into account the aberration of the thermal lens and considers it as an optical path length change to the probe laser beam, which can be expressed as an additional phase shift on the probe beam wave front after its passing through the sample. The analytical expression for absolute determination of the thermo-optical properties of the sample is given by [14–16]

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

In Eq. (1), $I(t)$ is the temporal dependence of the probe laser beam at the detector, $I(0)$ is the initial value of $I(t)$ (when the excitation beam is switched on), and θ is the difference between the thermally induced phase shift of the probe beam after its passing through the sample. The parameters m and V depend on the experimental arrangement, and t_c is the characteristic thermal lens time constant. The quantities m, V, θ, and t_c are related to the experimental and sample parameters through

$$\theta=-\frac{A_eP_eL}{\lambda_pk}\frac{dn}{dT}, \tag{2a}$$

$$m=\left(\frac{\omega_p}{\omega_e}\right)^2,\quad V=\frac{Z_1}{Z_C},\quad t_c=\frac{\omega_e^2}{4\alpha} \tag{2b}$$

ω_e and ω_p are the excitation and probe beam radii at the sample, and L is the sample thickness, as defined above. Furthermore, Z_1 is the position of the sample far from the probe beam waist and Z_C its confocal distance ($Z_C=\pi\omega_p^2/\lambda_p$), and dn/dT is the temperature coefficient of the sample refractive index at the probe beam wavelength λ_p. The other quantities in the equations above are the excitation beam power (P_e), absorption coefficient (A_e), sample thermal conductivity (k), and diffusivity (α).

In time resolved TL measurements, θ and t_c are straightforwardly obtained from the fitting of the experimentally observed time profile of the developing thermal lens to Eq. (1). In this procedure, $I(0)$, θ, and t_c are left as free parameters.

B. Refractive index

It is known from the literature that Vuks's equation [17,18] relates the microscopic structures of anisotropic liquid crystals to the indices of refraction as follows:

$$\left(\frac{n_i^2-1}{\langle n^2\rangle+2}\right)=\frac{R_i}{v}, \tag{3}$$

where n_i stands for $n_\parallel$ and $n_\perp$, the extraordinary and ordinary refractive indexes, $\langle n^2\rangle=(n_\parallel^2+2n_\perp^2)/3$ is the average value of the refractive index in the nematic phase, v is the molar volume, and R_i is the molar refractivity for a given polarization (parallel or perpendicular). The molar refractivity R_i is related to the electronic polarizability α_i through

$$R_i=\frac{N_A}{3\varepsilon_0}\alpha_i. \tag{4}$$

Here, N_A is Avogadro's number and ε_0 is the permittivity of free space. By differentiating Eq. (3) with respect to the temperature, we find

$$\frac{dn_i}{dT}=A_i(\phi_i-\beta)+B_i\frac{d\langle n^2\rangle}{dT}, \tag{5a}$$

where

$$A_i=\frac{(n_i^2-1)}{2n_i}\quad\text{and}\quad B_i=\frac{A_i}{\langle n^2\rangle+2}. \tag{5b}$$

The quantities ϕ_i and β are the temperature derivatives of the electronic polarizability and molar volume, the so called thermal expansion coefficient, respectively,

$$\phi_i=\frac{1}{R_i}\frac{\partial R_i}{\partial T}=\frac{1}{\alpha_i}\frac{\partial\alpha_i}{\partial T}, \tag{6a}$$

$$\beta=\frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_P. \tag{6b}$$

Resolving Eq. (5a) for the temperature coefficients of both the ordinary and extraordinary refractive indices, after a straightforward calculation we get

$$\frac{dn_\parallel}{dT}=p_\parallel(\phi_\parallel-\beta)-2q_\parallel(\phi_\parallel-\phi_\perp), \tag{7a}$$

$$\frac{dn_\perp}{dT}=p_\perp(\phi_\perp-\beta)+q_\perp(\phi_\parallel-\phi_\perp), \tag{7b}$$

and

$$p_i=\frac{(n_i^2-1)(\langle n^2\rangle+2)}{6n_i}>0, \tag{8a}$$

$$q_i=\frac{(n_\parallel^2-1)(n_\perp^2-1)}{18n_i}>0. \tag{8b}$$

Equations (7a) and (7b) will be used in interpretation of the TL results near the $I_{\mathrm{re}}\rightarrow N_C$ and $N_C\rightarrow I$ phase transitions.

IV. RESULTS AND DISCUSSION

Figure 1 shows the typical time resolved thermal lens signal in a homeotropic configuration (director aligned perpendicular to the sidewalls) for three different temperatures near the reentrant-isotropic–calamitic-nematic phase transition. An inversion can be observed in the build up of the thermal lens at 15.0 °C [Fig. 1(b)]: the self-defocusing behavior [Figs. 1(a) and 1(c)] observed for the entire range of temperature changed to a self-focusing one near the $I_{\mathrm{re}}\rightarrow N_C$ transition. The corresponding values of $\theta_\perp$ (normalized to the laser power) obtained from the phase-shift signal data fitting to Eq. (1) are plotted in Fig. 2, as a function of tem-

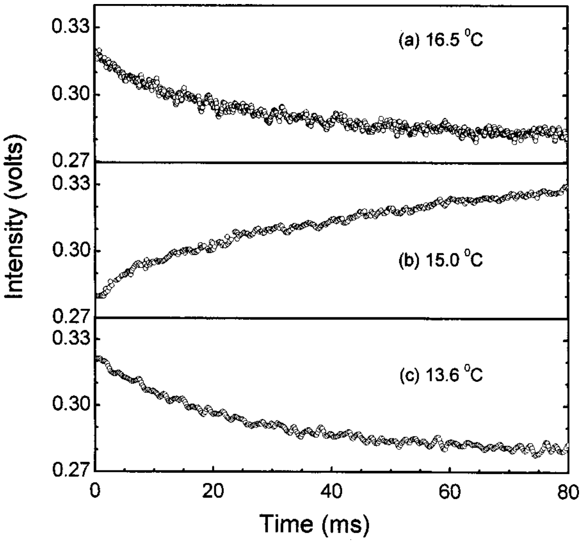

FIG. 1. TL experimental data and their best-fit curve: (a) reentrant isotropic phase; (b) near $T_{I\text{-}N_C}$; (c) nematic phase.

perature. Crosses in this figure represent the data points in the isotropic phase. They were obtained through an averaging of the data from all measurements performed in this region and showed to be reproducible. From Eq. (2a) one can see that all the parameters are positive, namely, the optical absorption coefficient and thermal conductivity etc., except dn/dT, which can be either positive or negative. Therefore, the occurrence of the sign change in θ (from positive to negative and vice versa) is related to dn/dT. As one can see from Fig. 2, $\theta_\perp$ is positive in the reentrant isotropic phase. As the temperature increases, $\theta_\perp$ decreases and becomes negative at 15.0 °C, returning to a positive value above 15.2 °C. It follows from Eq. (2a) that this inversion of the $\theta_\perp$ sign from positive to negative is a consequence of a change in $dn_\perp/dT$ from negative to positive. We note that this defocusing–self-focusing inversion was observed only near the $I_{\mathrm{re}} \rightarrow N_C$ phase transition, for the homeotropic geometry. Indeed, near the nematic-isotropic phase transition, $\theta_\perp$ increases with temperature, presenting a peak at 47.2 °C (see Fig. 2).

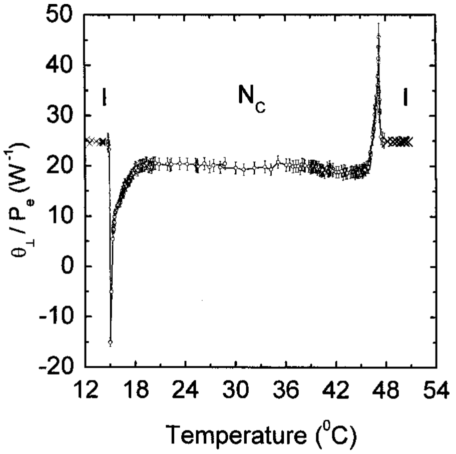

FIG. 2. Normalized probe beam phase shift $\theta_\perp/P_e$. Crosses represent θ/P_e in the isotropic phase.

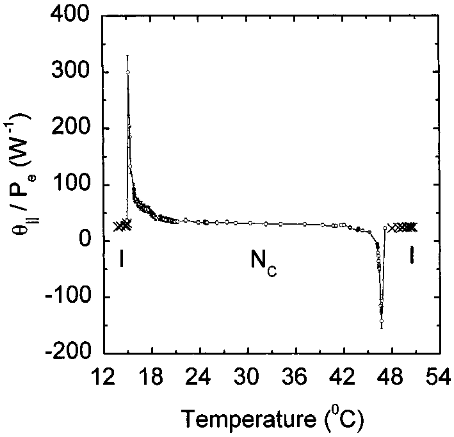

FIG. 3. Normalized probe beam phase shift $\theta_\parallel/P_e$. Crosses represent θ/P_e in the isotropic phase.

On the other hand, for the planar geometry, the sign of $\theta_\parallel$ does not change in the $I_{\mathrm{re}} \rightarrow N_C$ transition, as one can see in Fig. 3. For this geometry, $\theta_\parallel$ presents a peak at 15.2 °C, returning to an almost constant value in the range of the N_C phase. However, near the $N_C \rightarrow I$ phase transition, it decreases and becomes negative between 46.0 and 47.1 °C, reaching a minimum at 46.7 °C (see Fig. 3). This inversion of the $\theta_\parallel$ sign is a consequence of a change in $dn_\parallel/dT$ from negative to positive and was recently reported [12]. To our knowledge, except for our results reported in Ref. [12], there are no direct measurements of the behavior of dn/dT for lyotropic mixtures in the literature. A final remark on the experimental results is that the absolute values of $\theta_\parallel$ are much higher than those for $\theta_\perp$ near the phase transitions $(|\theta_\parallel| \gg |\theta_\perp|)$. According to Eq. (2a) this result leads to a variation of $n_\parallel$ much higher than the variation of $n_\perp$ in the phase transitions, since the anisotropy in the thermal parameters, specifically the thermal conductivity, is small for this system (see Ref. [10]). This variation of $n_\parallel$ is in accordance with refractive index measurements for a similar lyotropic system near the $N_C \rightarrow I$ phase transition [7].

Let us now consider Eqs. (7a) and (7b) in the analysis of the $dn_\perp/dT$ sign inversion in the $I_{\mathrm{re}} \rightarrow N_C$ transition. Taking the values of $n_\parallel$ and $n_\perp$ from Ref. [7] one can consider $p_\parallel \approx p_\perp = p$ and $q_\parallel \approx q_\perp = q$ [see Eqs. (8a) and (8b)]. Furthermore, $q \approx (p/13) \ll p$. Let us use these approximations and first discuss the birefringence in the nematic phase. Equation (7a) minus Eq. (7b) gives

$$\frac{d(n_\parallel - n_\perp)}{dT} = (p - 3q)(\phi_\parallel - \phi_\perp). \tag{9}$$

From Figs. 2 and 3, one deduces that $d(n_\parallel - n_\perp)/dT < 0$ around the $I_{\mathrm{re}} \rightarrow N_C$ phase transition. This result is also consistent with optical birefringence measurements performed on the same lyotropic mixture near these phase transitions [19]. Since $(p - 3q) > 0$, one concludes that

$$(\phi_\parallel - \phi_\perp) < 0 \quad \text{in the } I_{\mathrm{re}} \rightarrow N_C \text{ phase transition.} \tag{10a}$$

Conversely, the same analysis gives

$$(\phi_{\parallel}-\phi_{\perp})>0 \quad \text{in the } N_C \rightarrow I \text{ phase transition.} \tag{10b}$$

Therefore, going back to Eqs. (7a) and (7b), one concludes that the sign changes of $dn_{\parallel}/dT$ in the $I_{\mathrm{re}} \rightarrow N_C$ and of $dn_{\perp}/dT$ in the $N_C \rightarrow I$ transitions are associated with the variation of $\phi_{\parallel}$ and $\phi_{\perp}$. Our experimental results (Figs. 2 and 3) show that $\phi_{\perp}$ values dominate the inversion in the sign of $dn_{\perp}/dT$ occurring in the $I_{\mathrm{re}} \rightarrow N_C$ phase transition since $dn_{\perp}/dT$ becomes positive, indicating that $\phi_{\perp}$ prevails over β. In the same way, in the $N_C \rightarrow I$ transition $\phi_{\parallel}$ drives the inversion in the sign of the $dn_{\parallel}/dT$ values. These variations can be connected to some type of change in the micellar structure, such as those observed by x-ray diffraction measurements in a similar lyotropic system presenting a reentrant-isotropic–diskotic-nematic phase transition [20].

To sum up, a detailed study of the temperature derivative of the refractive indices near the reentrant-isotropic–calamitic-nematic phase transition was carried out. The results obtained for the $I_{\mathrm{re}} \rightarrow N_C$ phase transition were correlated with those previously reported for the $N_C \rightarrow I$ transition. The temperature coefficient of the electronic polarizability in the vicinity of the reentrant-isotropic–calamitic-nematic phase transition plays a relevant role in producing the sign change of $dn_{\perp}/dT$. The same occurs near the $N_C \rightarrow I$ transition for $dn_{\parallel}/dT$. A possible explanation of the observed behavior of dn/dT is a change in the shape of the micelles in the phase transitions. Furthermore, the observed inversion in dn/dT for both phase transitions ($I_{\mathrm{re}} \rightarrow N_C \rightarrow I$) shown in this work may be helpful for investigating, from a microscopic point of view, the influence of the temperature coefficient of the electronic polarizability of these materials over their nonlinear optical phenomena.

ACKNOWLEDGMENTS

We are thankful to the Brazilian agencies FAPESP, CAPES, and CNPq (PADCT) for the financial support of this work.

[1] P. G. de Gennes and J. Prost, *The Physics of Liquid Crystals*, 2nd ed. (Clarendon, Oxford, 1993).
[2] Y. Galerne and J. P. Marcerou, J. Phys. (Paris) **46**, 589 (1985).
[3] Y. Hendrikx, J. Charvolin, M. Rawiso, and M. C. Holmes, J. Phys. Chem. **87**, 3991 (1983).
[4] L. J. Yu and A. Saupe, Phys. Rev. Lett. **45**, 1000 (1980).
[5] K. C. Lim and J. T. Ho, Mol. Cryst. Liq. Cryst. **47**, 173 (1978).
[6] G. Vertogen and W. H. de Jeu, *Thermotropic Liquid Crystals* (Springer, Berlin, 1988).
[7] A. V. A. Pinto and A. A. Barbosa, Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A **309**, 45 (1998).
[8] Y. Galerne and J. P. Marcerou, Phys. Rev. Lett. **51**, 2109 (1983).
[9] S. L. Gómez, F. L. S. Guppo, A. M. Figueiredo Neto, T. Kosa, M. Muramatsu, and R. J. Horowicz, Phys. Rev. E **59**, 3059 (1999).
[10] A. C. Bento, A. J. Palangana, L. R. Evangelista, M. L. Baesso, J. R. D. Pereira, E. C. da Silva, and A. M. Mansanares, Appl. Phys. Lett. **68**, 3371 (1996).
[11] J. R. D. Pereira, A. M. Mansanares, A. J. Palangana, and M. L. Baesso, Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A **332**, 3079 (1999).
[12] J. R. D. Pereira, A. J. Palangana, A. M. Mansanares, A. C. Bento, E. C. da Silva, and M. L. Baesso, Phys. Rev. E **61**, 5410 (2000).
[13] T. Kroin and A. M. Figueiredo Neto, Phys. Rev. A **36**, 2987 (1987).
[14] S. Jun, R. D. Lowe, and R. D. Snook, Chem. Phys. **165**, 385 (1992).
[15] J. Shen, M. L. Baesso, and R. D. Snook, J. Appl. Phys. **75**, 3738 (1994).
[16] M. L. Baesso, J. R. D. Pereira, A. C. Bento, A. J. Palangana, A. M. Mansanares, and L. R. Evangelista, Braz. J. Phys. **28**, 359 (1998).
[17] M. F. Vuks, Opt. Spectrosk. **20**, 644 (1966) [Opt. Spectrosc. **20**, 361 (1966)].
[18] I. C. Khoo and S. T. Wu, *Optics and Nonlinear Optics of Liquid Crystals* (World Scientific, Singapore, 1993).
[19] A. M. Ribas, L. R. Evangelista, A. J. Palangana, and E. A. Oliveira, Phys. Rev. E **51**, 5204 (1995).
[20] Y. Galerne, A. M. Figueiredo Neto, and L. Liebét, Phys. Rev. A **31**, 4047 (1985).