PHYSICAL REVIEW E, VOLUME 65, 057602

Refractive index measurements in a reentrant isotropic-calamitic nematic phase transition

P. A. Santoro, J. R. D. Pereira, and A. J. Palangana*
Departamento de Física, Universidade Estadual de Maringá, Avenida Colombo, 5790, 87020-900 Maringá, PR, Brazil

(Received 7 November 2001; published 17 May 2002)

In this work the temperature dependence of the extraordinary/ordinary refractive indices and optical birefringence are determined near the reentrant isotropic (I_{RE})-calamitic nematic (N_C) and N_C-isotropic (I) phase transitions in a lyotropic mixture of potassium laurate, decanol, and water. This reentrant isotropic phase is verified by our experimental data and discussed in terms of thermal variation of the micellar shape anisotropy. The results showed also, with basis in the Vuks's equation, that near the maximum optical birefringence in the range of N_C phase the extraordinary coefficient of electronic polarizability ($\phi_\parallel$) is equal to the ordinary coefficient ($\phi_\perp$).

DOI: 10.1103/PhysRevE.65.057602 PACS number(s): 42.70.Df, 61.30.−v, 64.70.Md, 42.65.Jx

I. INTRODUCTION

The optical characterization of uniaxial nematic liquid crystals requires the measurements of two refractive indices, the ordinary (n_o) and extraordinary (n_e) defined, respectively, for plane waves traveling in the nematic medium with polarization perpendicular or parallel to the optic axis of the nematic sample. The optical birefringence $\Delta n = n_e - n_o = n_\parallel - n_\perp$, is a fundamental macroscopic order parameter, related to the microscopic order parameter of the nematic phase [1,2]. Extraordinary and ordinary refractive indices have been seldom investigated, particulary in lyotropic liquid crystals (LC). These systems are formed by mixtures of amphiphilic molecules and a solvent (usually water), under convenient temperature and concentration conditions. The basic units of the LC are anisotropic micelles [3]. In the temperature-concentration phase diagram, two uniaxial and one biaxial nematic phases have been observed [4]. The uniaxial nematic phases have been shown to be prolate (calamitic N_C) and oblate (discotic N_D) micellar aggregates dispersed in water [3]. The biaxial nematic phase (N_B) appears to be an intermediate phase along the border between the two uniaxial nematic ones. From the phase diagram studied by Yu and Saupe [4], the occurrence of the reentrant isotropic phase was pointed out by these authors and is investigated in this work.

Using the refractometry technique we report on measurements of the extraordinary ($n_\parallel$) and ordinary ($n_\perp$) refractive indices near the reentrant isotropic (I_{RE})-calamitic nematic (N_C) and N_C-isotropic (I) phase transitions, as a function of temperature in a lyotropic mixture of potassium laurate, decanol, and water. The optical birefringence, near these phase transitions, is also determined as a function of temperature. In this sense we show, via the temperature derivative of the Vuks's equation [5], that the extraordinary and ordinary coefficients of the electronic polarizability (ϕ_i) are equal at the point where the optical birefringence reaches the maximum value in the range of calamitic nematic phase.

II. EXPERIMENT

The lyotropic mixture investigated in this work was prepared with the following concentrations in weight percent; potassium laurate (KL: 29.4), decanol (DeOH: 6.6), and water (64.0). The phase sequences were determined by optical microscopy and conoscopic observations, which have shown that it is I_{RE} up to 11.0 °C, being that the N_C phase upon heating changes to the isotropic (I) phase at 47.0 °C. Temperature dependences of extraordinary and ordinary refractive indices, near the I_{RE}-N_C and N_C-I phase transitions, were performed through an Abbe refractometer ($Atago-3T$) with an accuracy of 2×10^{-4} and the sample temperature control was stable within 0.01 K. The nematic sample was prepared in sealed planar cells (length 44 mm, width 12.5 mm, and 1.0 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. Initially the sample nematic is oriented with the director **n** parallel to the x axis by applying a magnetic field of 10 kG for some hours at room temperature. When a good planar alignment is achieved, the nematic sample is removed from the electromagnet and placed in the Abbe refractometer. In these measurements, the aligned sample was treated as a solid [6] and for optical coupling Canada balsam was used ($n=1.530$). An optical polarization dispositive was coupled to the optical system of the Abbe refractometer in order to get the extraordinary and ordinary refractive index measurements.

III. RESULTS AND DISCUSSION

The extraordinary ($n_\parallel$) and ordinary ($n_\perp$) refractive indices as functions of temperature are presented in Fig. 1. As one sees from Fig. 1, near the reentrant isotropic-calamitic nematic phase transition, $n_\perp(n_\parallel)$ decreases (increases) as the temperature decreases until, in the reentrant isotropic phase, just one refractive index was determined. This fact confirms the existence of the reentrant isotropic phase in accordance to the phase diagram proposed by Yu and Saupe [4]. On the other hand, near the N_C-I phase transition, as the temperature increases $n_\perp(n_\parallel)$ decreases (increases), and in this way both indices trend to one index in the isotropic phase. Full stars in this figure represent the values of $\langle n\rangle$ where $\langle n^2\rangle = (n_\parallel^2$

---

*Email address: palanga@dfi.uem.br

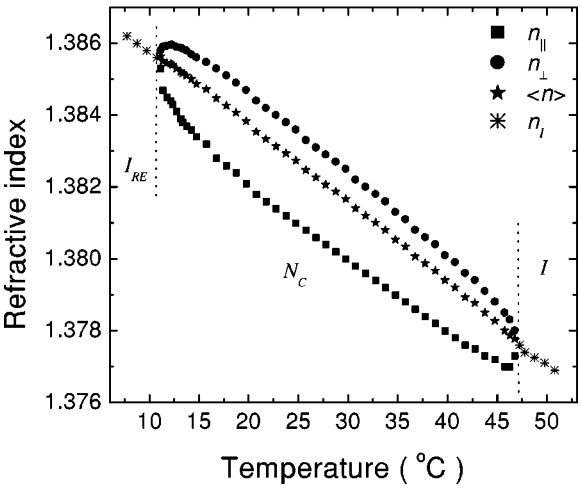

FIG. 1. Extraordinary ($n_\parallel$) and ordinary ($n_\perp$) refractive indices versus temperature of KL system, for sodium D line (589.3 nm). I_{RE}, N_C, and I are the isotropic reentrant, calamitic nematic, and isotropic phases, respectively.

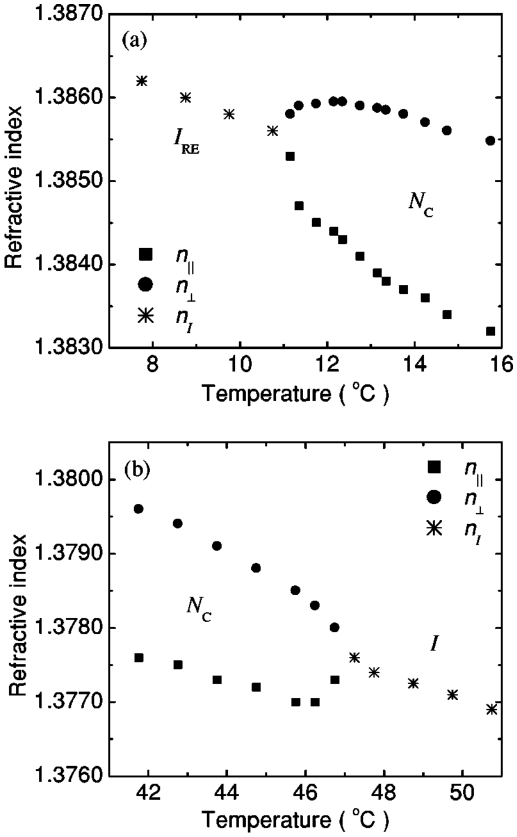

FIG. 2. Extraordinary ($n_\parallel$) and ordinary ($n_\perp$) refractive indices of KL system versus temperature; (a) near the reentrant isotropic-calamitic nematic phase transition and (b) near the calamitic nematic-isotropic phase transition.

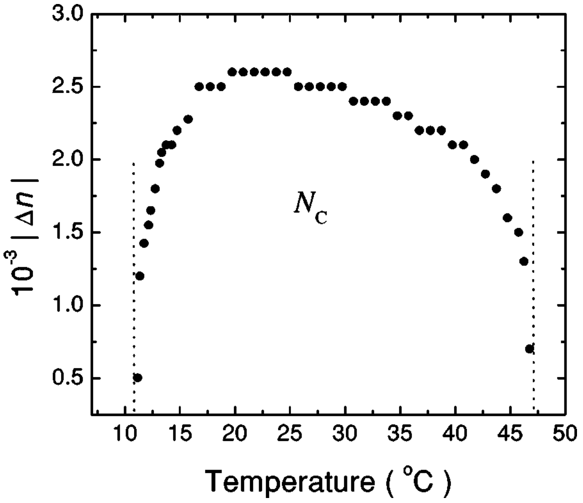

FIG. 3. Birefringence (Δn) as a function of the temperature of KL system in the calamitic nematic phase.

$+2n_\perp^2)/3$ is the averaged value of the refractive index in the calamitic nematic phase. In the isotropic phases $\langle n\rangle = n_i$ is the measured refractive index [7]. Figure 2 shows a magnified view of the extraordinary and ordinary refractive indices in the vicinities of I_{RE}-N_C and N_C-I phase transitions. To our knowledge, there are no direct measurements of the $n_\parallel(n_\perp)$ refractive index for this lyotropic mixture in the literature. From the experimental results of extraordinary and ordinary refractive indices one gets the optical birefringence Δn that is negative in this calamitic nematic sample. A similar result for Δn, for this lyotropic mixture, was obtained by another experimental technique [8]. The absolute values of Δn as a function of temperature in the N_C phase of the KL lyotropic mixture are plotted in Fig. 3. We note that, near the I_{RE}-N_C phase transition Δn increases in absolute value and becomes maximum around 22.0 °C and subsequently decreases as the temperature increases. Using the Vuks's equation [5] it can be shown that the temperature derivatives of the refractive index dn_i/dT can be written as [9]

$$\frac{dn_i}{dT}=a_i(\phi_i-\beta)+b_i\frac{d\langle n^2\rangle}{dT}, \tag{1}$$

where n_i stands for $n_\parallel(n_\perp)$, as the extraordinary (ordinary) refractive index, $d\langle n^2\rangle/dT$ is the temperature derivative of the averaged value of the refractive index in the nematic phase, $\phi_i=(1/R_i)(dR_i/dT)$ is the coefficient of the electronic polarizability [10], R_i is the molar refractivity, $a_i=(n_i^2-1)/2n_i$, $b_i=a_i/(\langle n^2\rangle+2)$, $\beta=(1/v)\ (\partial v/\partial T)_P$ is the thermal expansion coefficient, and v is the molar volume. Writing Eq. (1) for the extraordinary/ordinary refractive indices and using $\Delta n=n_\parallel-n_\perp$, one gets

$$\frac{d(\Delta n)}{dT}=a_\parallel\phi_\parallel-a_\perp\phi_\perp-\beta(a_\parallel-a_\perp)+(b_\parallel-b_\perp)\frac{d\langle n^2\rangle}{dT}, \tag{2}$$

where $\phi_\parallel(\phi_\perp)$ is the extraordinary (ordinary) coefficient of the electronic polarizability. Let us consider Eq. (2) in the condition for the maximum optical birefringence. In this case, $d(\Delta n)/dT=0$ at temperature $T\simeq 22.0$ °C. Taking into account the experimental values $a_\parallel=0.329$, $b_\parallel=0.084$, $a_\perp=0.331$, $b_\perp=0.085$, $d\langle n^2\rangle/dT=(-6.060\times10^{-4})\ ^\circ\mathrm{C}^{-1}$ and $\beta=(5.348\times10^{-4})\ ^\circ\mathrm{C}^{-1}$ from Ref. [11], we obtain $\phi_\parallel\simeq\phi_\perp$

$=(5.035\times 10^{-4})\ ^{\circ}\mathrm{C}^{-1}$. This is an important result and shows that the strength of the molecular polarizability of this particular nematic sample, at this singular point where the optical birefringence is maximum, is the same in the direction of the nematic director or perpendicular to it. In fact, this result is not so surprising as it may look at a first glance since the existence of the reentrant isotropic phase is verified by our experimental data. The reentrant transition, particulary in the lyotropic mixture, has been attributed to the temperature-dependent interaction associated with the thermal variation in the shape anisotropy of the micelles [12]. This argument is consistent with x-ray diffraction experiments showing a micellar shape change near the reentrant isotropic-discotic nematic (N_D) and N_D-I phase transitions in a lyotropic mixture [13].

To sum up, we have carried out a detailed refractive index study near the I_{RE}-N_C and N_C-I phase transitions of a lyotropic calamitic nematic phase. The experimental results are consistent with the phase diagram proposed by Yu and Saupe [4] and confirms the occurrence of the reentrant isotropic phase. We have shown, via the temperature derivative of the Vuks's equation [5], that the extraordinary and ordinary coefficients of the electronic polarizability (ϕ_i) are equal at the point where the optical birefringence reaches the maximum value in the range of calamitic nematic phase. Finally, we mention that similar experiments in a reentrant isotropic-discotic nematic phase transition are in progress.

ACKNOWLEDGMENTS

We are thankful to the Brazilian Agencies CAPES and CNPq (PADCT) for the financial support of this work. Many thanks are due to G. J. Vidotti (Brazil) for his kind assistance in the synthesis of the potassium laurate.

---

[1] P.G. de Gennes and J. Prost, *The Physics of Liquid Crystals*, 2nd ed. (Clarendon Press, Oxford, 1993).
[2] G. Vertogen and W.H. de Jeu, *Thermotropic Liquid Crystal* (Verlag, Berlin, 1988).
[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] M.F. Vuks, Opt. Spectrosc. **20**, 361 (1966).
[6] A.V.A. Pinto and A.A. Barbosa, Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A **309**, 45 (1998).
[7] I. Haller, H.A. Huggins, and M.J. Freiser, Mol. Cryst. Liq. Cryst. **16**, 53 (1972).
[8] A.M. Ribas, L.R. Evangelista, A.J. Palangana, and E.A. de Oliveira, Phys. Rev. E **51**, 5204 (1995).
[9] J.R.D. Pereira, A.M. Mansanares, A.J. Palangana, and M.L. Baesso, Phys. Rev. E **64**, 012701 (2001).
[10] L. Prod'homme, Phys. Chem. Glasses **1**, 119 (1960).
[11] P.A. Santoro, J.R.D. Pereira, and A.J. Palangana, Mol. Cryst. Liq. Cryst. **375**, 387 (2002).
[12] M.J. de Oliveira and A.M. Figueiredo Neto, Phys. Rev. A **34**, 3481 (1986).
[13] Y. Galerne, A.M. Figueiredo Neto, and L. Liébert, Phys. Rev. A **31**, 4047 (1985).