Temperature dependence of the coefficient of electronic polarizability in calamitic nematic liquid crystals

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In this report the temperature dependence of the coefficient of electronic polarizability (ϕ_i) is determined by means of the thermal expansion coefficient (β) and ordinary/extraordinary refractive indexes measurements near the calamitic nematic-isotropic phase transition in a lyotropic mixture of sodium decylsulphonate, decanol, and water. These parameters (ϕ_i and β) were related to the extraordinary and ordinary refractive indexes via the temperature derivative of the Vuks's equation. The results showed that near the nematic-isotropic phase transition, the measured value of ϕ_i was found to be about two orders of magnitude smaller than that obtained for thermotropic, showing a remarkable difference in the molecular electronic polarizability strength between lyotropic and thermotropic liquid crystals.

I. INTRODUCTION

The investigation of the optical properties in liquid crystals (LC) is one of the most interesting research topics, not only from the fundamental point of view but also for technological applications [1]. Despite the recent growing interest on lyotropic liquid crystals, the data in the literature regarding the basic physical properties of these systems are scarce. Lyotropic LC are formed by mixtures of amphiphilic molecules and a solvent (usually water), under convenient temperature and concentration conditions. The basic units of these systems are anisotropic micelles [2]. In the temperature-concentration phase diagram, two uniaxial and one biaxial nematic phases have been observed [3]. The biaxial nematic phase (N_B) appears to be an intermediate phase along the border between the two uniaxial nematic ones. The uniaxial nematic phases have been shown to be prolate (calamitic-N_C) and oblate (discotic-N_D) micellar aggregates dispersed in water [2]. Measurements of the extraordinary ($n_\parallel$) and ordinary ($n_\perp$) refractive indexes and thermal expansion coefficient (β) as a function of temperature are very important parameters to study the phase transition in liquid crystals. These parameters can be related, via the temperature derivative of the Vuks's equation, with the coefficient of the electronic polarizability (ϕ_i). This coefficient reflects from a microscopic point of view, the nature of the sample molecular polarizability, and is associated with the electronic polarizing power Z/a^2, where a is the distance between the dipole charges (Z). The determination of ϕ_i values is relevant since it provides information about the nonlinear optical response of these systems. To our knowledge, the absolute value of the coefficient of the electronic polarizability in lyotropic liquid crystals has not yet been measured. In this paper we report a method to determine ϕ_i as a

function of the temperature in a lyotropic liquid crystal mixture near the calamitic nematic-isotropic phase transition, using the refractometry and densitometry techniques.

II. FUNDAMENTALS

It is know from the literature that the Vuks's equation relates the microscopic structures of liquid crystal molecules to the index of refraction as follows [4–6]:

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

where n_i stands for $n_\parallel(n_\perp)$, as the extraordinary (ordinary) refractive index, $\langle n^2 \rangle = (n_\parallel^2 + 2n_\perp^2)/3$ is the averaged value of the refractive index in the nematic phases, v is the molar volume, and R_i is the molar refractivity. Differentiating Eq. (1) with respect to the temperature, the parameter ϕ_i can be written as follows [7]:

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

where $a_i = (n_i^2 - 1)/2n_i$, $b_i = a_i/(\langle n^2 \rangle + 2)$, $\phi_i = 1/R_i(dR_i/dT)$ is the coefficient of the electronic polarizability, and $\beta = 1/v(\partial v/\partial T)_P$ is the thermal expansion coefficient. Equation (2) is the working equation, which will be used in the sequence to determine the coefficient ϕ_i of a lyotropic mixture of sodium decylsulphonate, decanol, and water near the nematic calamitic-isotropic phase transition.

The lyotropic mixture investigated in this report was prepared with the following concentrations in weight percent: sodium decylsulphonate (SDS_{NATE}:37.6), decanol (DeOH:8.0), and water (54.4). The nematic calamitic phase (N_C) upon heating changes to the isotropic (I) phase at 43.5 °C [8]. The thermal expansion coefficient $\beta = -1/\rho(\partial\rho/\partial T)_P$ as a function of temperature was obtained from density experimental data, near the calamitic nematic-
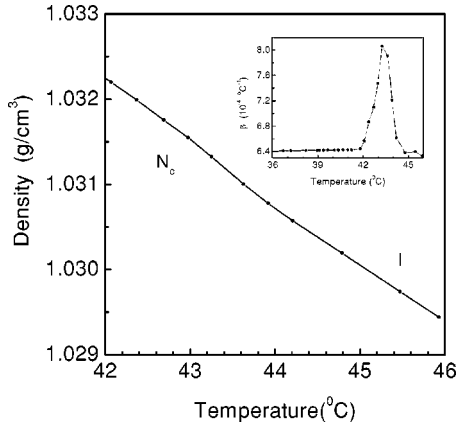
FIG. 1. Density as a function of temperature near the calamitic nematic-isotropic phase transition in the SDS_{NATE} system. The inset shows the thermal-expansion coefficient as a function of temperature near the calamitic nematic-isotropic phase transition in the SDS_{NATE} system.
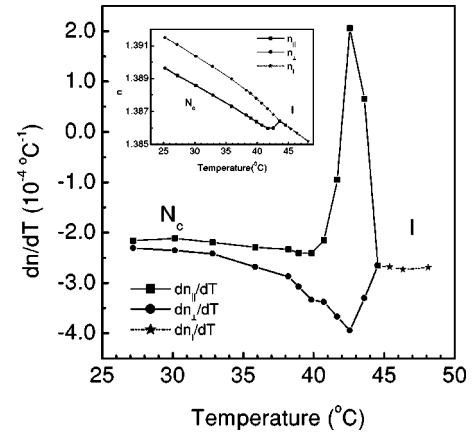

FIG. 2. Temperature derivative of the ordinary and extraordinary refractive indexes vs temperature at calamitic nematic-isotropic phase transition in the SDS_{NATE} system. The inset shows the extraordinary and ordinary refractive indexes [8] vs temperature at calamitic nematic-isotropic phase transition in the SDS_{NATE} system.

isotropic phase transition. Density measurements were determined [9] through the oscillation period of a U-shaped tube by means of an Anton Paar instrument consisting of a microcell direct memory access (DMA-602HT) and a processing unit (DMA-60). The sample temperature was controlled by a Haake $K-20/DC-5$ circulating temperature bath. The temperatures of the sample were stable at 0.01 K. The densimeter calibration constant was determined from the known values of the water and the air [10,11]. Special care was taken during the experiments in such a way that no air bubbles were presented in the liquid-crystalline samples. The precision of the densimeter is 5×10^{-6} g/cm³. For these experiments, the samples were contained in a U-shaped tube with internal diameter of 2 mm. The curve part of the sample tube was electronically stimulated in an undamped harmonic fashion. The direction of oscillation was perpendicular to the plane of the U-shaped sample tube. The U-shaped tube was clamped so that the vibration amplitude was larger in the curved part of the tube. Then, the phase transition temperatures were checked from the bulk of the sample tube by using a polarized light microscope

III. RESULTS AND DISCUSSION

The density and thermal-expansion coefficient as a function of temperature are presented in Fig. 1. It can be observed that the density decreases as the temperature increases. An additional change in the density values can be observed around 43.5 °C, where the N_C-isotropic phase transition occurs. The inset of Fig. 1 shows the thermal-expansion coefficient results that were obtained through the derivative of the density values. The results show that temperature range of the phase transition in our sample is of the order 1 °C. From optical microscopy measurements, we also observed the same width of the transition. These results indicate a possible coexistence of N_C-isotropic phases at the temperature range where the transition occurs. In fact, this result is not as surprising as it may look at a first glance since

the coexistence of phases has also been observed in other lyotropic liquid crystal systems [12–14].

Measurements of the extraordinary ($n_\parallel$) and ordinary ($n_\perp$) refractive indexes as a function of temperature, near the calamitic nematic-isotropic phase transition, were performed through Abbe refractometer [8] and their respective temperature derivative $dn_\parallel(n_\perp)/dT$ are shown in Fig. 2. We note that, near the N_C-isotropic phase transition and for the planar configuration, $dn_\parallel/dT$ increases from negative values and become positive between 42 °C and 43.5 °C, returning to a negative value above 43.5 °C. This inversion of the $dn_\parallel/dT$ sign, was also recently observed [15] by means of a thermal lens technique [16], in another lyotropic mixture of potassium laurate, decanol, and water near the calamitic nematic-isotropic phase transition. This effect was attributed to an increase of the electronic polarizability due to a change in the micelle shape near this phase transition.

In order to further explore the dn/dT data shown in Fig. 2, we have used Eq. (2) to determine the temperature dependence of the ϕ_i values near the N_C-isotropic phase transition. The obtained results are shown in Fig. 3. We should remark that the order of magnitude of ϕ_i determined in this report for lyotropic LC is the same as that obtained for water by Colcombe *et al.* [17]. For the planar (homeotropic) geometry, one may note a well-defined peak in the $\phi_\parallel(\phi_\perp)$ values at the calamitic nematic-isotropic phase transition, where in absolute values $\phi_\parallel>\phi_\perp$. This increase in the $\phi_\parallel$ values in the long axis of the micelles, near the N_C-isotropic phase transition, agrees with the observation that in the nematic-isotropic phase transition, in thermotropic liquid crystals, the electronic polarizability is greatly enhanced on the axis parallel to the director [5,18]. As ϕ_i is related with the electronic polarizing power Z/a^2, a decrease in the ratio Z/a^2 means a decrease in the atomic group size, producing a consequent increase in the value of these polarizing groups [15], near the nematic-isotropic phase transition as compared to the nematic and isotropic phases. In this sense, in [5,19] the
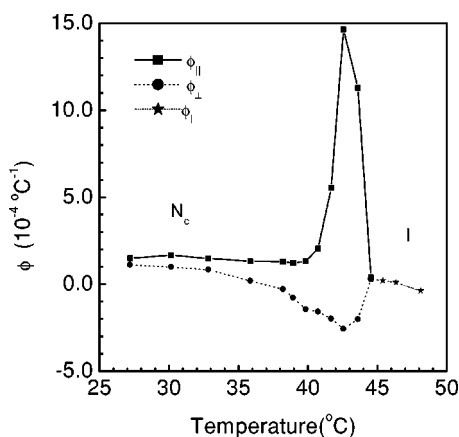
FIG. 3. Coefficient of the electronic polarizability vs temperature at calamitic nematic-isotropic phase transition in the SDS_{NATE} system.

FIG. 4. Coefficient of the electronic polarizability vs temperature at nematic-isotropic phase transition in the MBBA system.

thermal expansion coefficient and ordinary and extraordinary refractive indexes have been measured as a function of the temperature, for the nematic thermotropic-MBBA. From these experimental data, it is possible to obtain, via Eq. (2), the coefficient of the electronic polarizability ϕ_i in the vicinity of the nematic-isotropic phase transition, shown in Fig. 4. On the other hand, in the range of the nematic phase, the ratio $\phi_{\parallel}/\phi_{\perp}$ is approximately the same, for both lyotropic and thermotropic systems studied in this report. However, the magnitude of the coefficient of the electronic polarizability ϕ_i, at nematic-isotropic phase transition in thermotropic is about 10^2 times higher than the ϕ_i values measured at the calamitic nematic-isotropic phase transition in lyotropic. This is a fundamental result and shows clearly the difference between the two systems in terms of the strength of their molecular electronic polarizability. It is important to remember that the thermotropic liquid crystals differ from the micellar systems as the lyotropics, which are complex structures consisting of mixtures of amphiphilic molecules and a solvent.
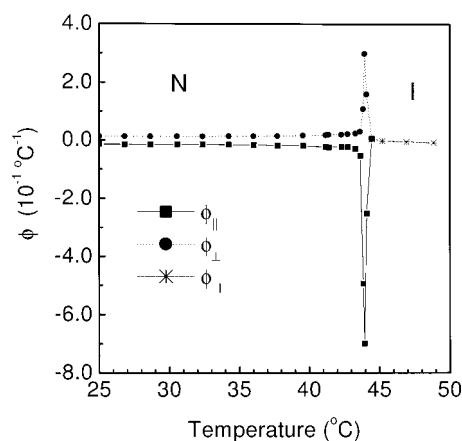
To sum up, we have developed a method to measure the temperature dependence of the coefficient of the electronic polarizability of a lyotropic calamitic nematic phase. This coefficient reveals the strength of the molecular polarizability of this system. The method uses the Vuks's equation that relates the thermal expansion coefficient and ordinary and extraordinary refractive indexes. We have shown that the order of magnitude of ϕ_i in nematic thermotropic is two times larger than that of the nematic lyotropic. Finally, considering that the optical and orientational properties of lyotropics are greatly modified when a small amount of ferrofluid is introduced into its composition, our results indicate that the experimental procedure adopted in this report may be useful to investigate this ferronematic system. Additional experiments, in this way, with other micellar systems are in progress.

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