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Reentrant isotropic–discotic nematic lyotropic phase transition: a refractive index study

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In this work the temperature dependence of the extraordinary/ordinary refractive indices and the optical birefringence are determined near the reentrant isotropic–discotic nematic–isotropic phase transitions for a lyotropic mixture of potassium laurate, decanol and D_2O. These parameters are related to the extraordinary/ordinary molar refractivity through Vuks's equation and discussed in terms of structural changes in the micellar configuration at the transitions.

1. Introduction

Lyotropic liquid crystals are formed by mixtures of amphiphilic molecules and a solvent (usually water), under the appropriate temperature and concentration conditions. The basic units of these systems are anisotropic micelles, and several lyotropic phases have been investigated [1–5]. In the temperature–concentration phase diagram for the ternary system potassium laurate, 1- decanol and D_2O, studied by Yu and Saupe [3], two uniaxial and one biaxial nematic phases were observed. The uniaxial nematic phases are known as calamitic (N_C) and discotic (N_D), depending on their optical and diamagnetic anisotropy [5]. The N_C (N_D) nematic lyotropic phases exhibit negative (positive) optical and positive (negative) diamagnetic anisotropies. The biaxial nematic phase (N_B) appears to be an intermediate phase appearing at the border between the two uniaxial nematic phases. However, the existence of this biaxial nematic lyotropic phase remains an open question [6]. For particular concentrations of the three components the phase diagram [3] also contains the phase sequence: reentrant isotropic (I_{RE})–N_D–isotropic (I). In lyotropic liquid crystals the extraordinary (n_e) and ordinary (n_o) refractive indices have been the focus of few investigations. Thus in this paper these refractive indices are determined as a function of temperature near I_{RE}–N_D–I phase transitions, using the refractometry technique. The optical birefringence $\Delta n = n_e – n_o = n_\parallel – n_\perp$, a relevant macroscopic order parameter, is also determined as a function of temperature near these phase transitions. These parameters are related to the extraordinary/ordinary molar refractivity through Vuks's equation [7]. The existence of the reentrant isotropic phase is verified by our experimental data and discussed in terms of a thermal variation of the micellar shape anisotropy.

2. Experimental

The lyotropic mixture investigated in this work was prepared with the following concentrations (weight percent): potassium laurate (KL: 24.80), decanol (DeOH: 6.24) and (D_2O: 68.96). The phase sequence, determined by optical measurements, is reentrant isotropic (I_{RE}) up to 12.1°C, discotic nematic (N_D) from 12.1 to 36.3°C, and isotropic (I) above 36.3°C. Extraordinary and ordinary refractive index measurements, near the I_{RE}–N_D and N_D–I phase transitions, were performed using an Abbe refractometer (Atago-3T) with an accuracy of 2×10^{-4}, and sample temperature control was stable to 0.01 K. The nematic sample was prepared in sealed planar glass cells ($n_g = 1.523$) from Hellma with 1.0 mm of light path. The xy-plane of the sample is defined with the x(y) axis parallel to the length (width) of the cells. Homeotropic alignment of the sample, at room temperature, was produced by a magnetic field of 10 kG parallel to the x-axis of the laboratory frame combined with rotations of the sample around an axis perpendicular to the magnetic field (z-axis). On achieving a good homeotropic alignment, the nematic sample was removed from the electromagnet and placed on the Abbe refractometer [8, 9]. We used Canada balsam ($n = 1.537$) as the optical coupling and the sodium D

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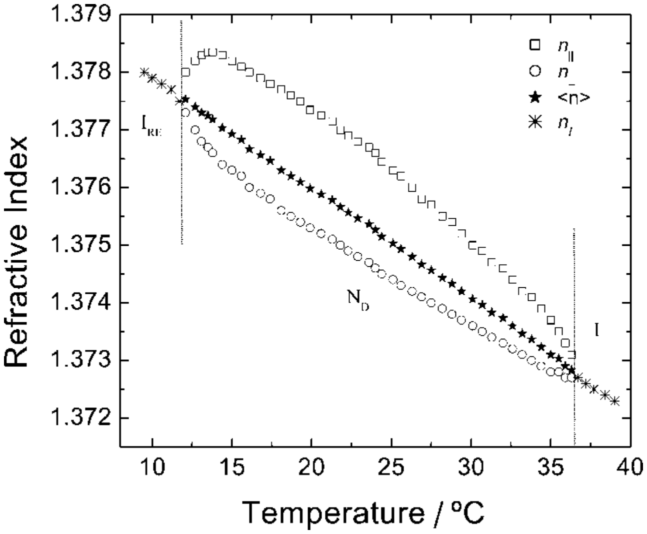

Figure 1. Extraordinary ($n_{\parallel}$) and ordinary ($n_{\perp}$) refractive indices vs temperature for the KL system, for the sodium D line ($\lambda = 589.3$ nm).

line ($\lambda = 589.3$ nm). In this experiment $n_e(n_o) < n_g < n$. The refractive index measurements using this refractometer are based on the internal reflection of light at the interface between the nematic sample and the surface of an optical glass prism. An optical polarizer was coupled to the Abbe refractometer in order to obtain the extraordinary and ordinary refractive index measurements.

3. Results and discussion

Figure 1 shows the extraordinary ($n_{\parallel}$) and ordinary ($n_{\perp}$) refractive indices as a function of temperature near the $\mathrm{I_{RE}}$–$\mathrm{N_D}$ and $\mathrm{N_D}$–I phase transitions and in the range of the discotic nematic phase. Note that from figure 1, near the $\mathrm{I_{RE}}$–$\mathrm{N_D}$ phase transition, $n_{\parallel}(n_{\perp})$ decreases (increases) when the temperature decreases and, in the $\mathrm{I_{RE}}$ phase, just one refractive index was determined. This confirms the existence of the reentrant isotropic phase in accordance with the phase diagram proposed by Yu and Saupe [3, 10]. On the other hand, near the $\mathrm{N_D}$–I phase transition, when the temperature increases $n_{\parallel}(n_{\perp})$ decreases (increases). In the isotropic phase the extraordinary and ordinary refractive indices become a single refractive index. Filled stars in figure 1 represent the average value of the refractive index, $\langle n\rangle$, obtained [11] from the relationship $\langle n^2\rangle = \left(n_{\parallel}^2 + 2n_{\perp}^2\right)/3$, in the discotic nematic phase.

Figure 2 shows a detailed plot of the extraordinary and ordinary refractive indices in the vicinities of the $\mathrm{I_{RE}}$–$\mathrm{N_D}$–I phase transitions. To our knowledge, there are no previous measurements of the $n_{\parallel}$ and $n_{\perp}$ refractive indices for this phase sequence shown by this lyotropic mixture. Recently, we reported [9] the use of the same technique for the measurement of the extraordinary and ordinary refractive indices, in a similar lyotropic mixture, near the $\mathrm{I_{RE}}$–calamitic nematic ($\mathrm{N_C}$)–I phase transition. From the extraordinary and ordinary refractive indices one obtains the optical birefringence Δn, which is positive in this discotic nematic phase and negative in the calamitic nematic phase [9].

In this sense, our experimental results when compared with the figure 1 shown in [9] reflect this fact by means of an inversion by symmetry in the behaviour of the refractive indices. The experimental values of Δn as a function of temperature in the $\mathrm{N_D}$ phase of the

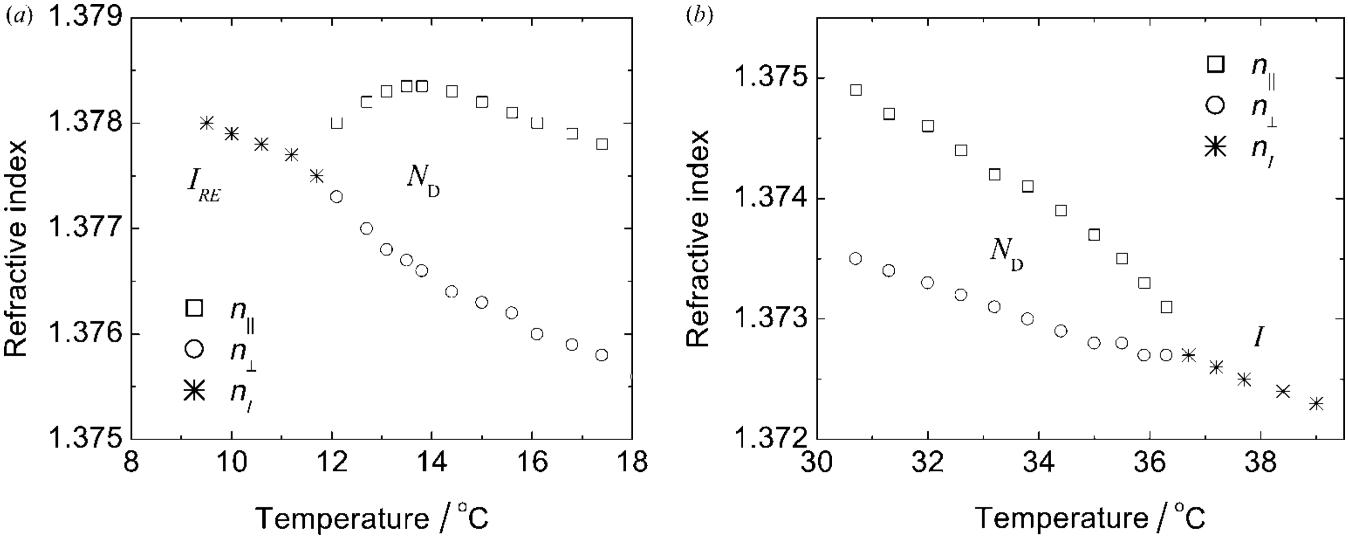

Figure 2. Extraordinary ($n_{\parallel}$) and ordinary ($n_{\perp}$) refractive indices of the KL system vs temperature: (*a*) near the $\mathrm{I_{RE}}$–$\mathrm{N_D}$ phase transition; (*b*) near the $\mathrm{N_D}$–I phase transition.

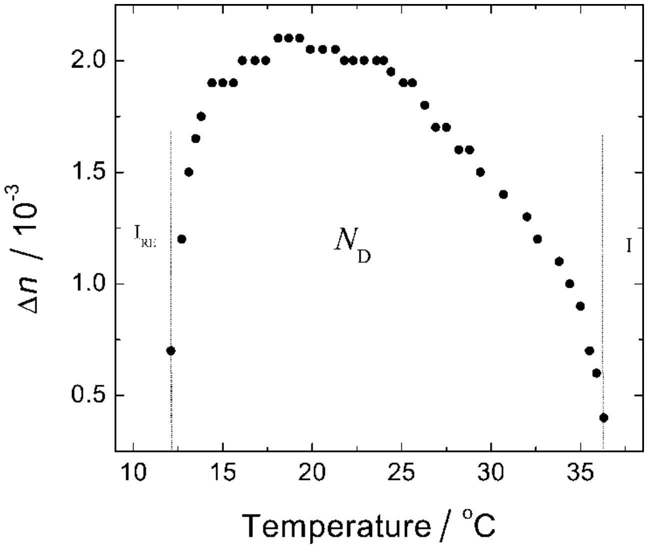

Figure 3. Birefringence (Δn) as a function of temperature for the KL system in the discotic nematic phase.

KL lyotropic mixture are plotted in figure 3. We note that near the I_{RE}–N_D phase transition Δn increases in value, has a maximum value at around 19.0°C and subsequently decreases as the temperature increases. A similar result for Δn, for this lyotropic mixture, was obtained using a laser conoscopy technique [12].

By using Vuks's equation $R_i/v = (n_i^2 - 1)/(\langle n^2\rangle + 2)$, relating the microscopic structures [7, 13] (molar refractivity R_i and molar volume v) of liquid crystal molecules to the macroscopic parameter (refractive index n_i) we obtain [14]

$$R_i = (n_i^2 - 1)/(\langle n^2\rangle + 2)(M/\rho) \qquad (1)$$

where n_i is the $n_{\parallel(\perp)}$ extraordinary (ordinary) refractive index, $\langle n^2\rangle = \left(n_\parallel^2 + 2n_\perp^2\right)/3$ is the average value of the refractive index in the nematic phase, M is the molecular mass and ρ the density. Density measurements in the N_D phase and near the I_{RE}–N_D and N_D–I phase transitions were made, with an accuracy of $5\times10^{-6}\,\mathrm{g\,cm^{-3}}$, using an Anton Paar instrument (densimeter) [15] consisting of a microcell (DMA-602HT) and a processing unit (DMA-60). The sample temperature was controlled by a Heto CB8-30E/DT circulating temperature bath, ensuring that the temperature readings were stable to 0.01 K.

Density values, as a function of temperature near the I_{RE}–N_D and N_D–I phase transitions, are shown in figure 4. Note that the density decreases as temperature increases. Furthermore, a very small change in the density value was observed around the phase transitions. Similar results were observed in other lyotropic mixtures [16, 17]. Taking into account the experimental values of the parameters n_i^2, $\langle n^2\rangle$ and ρ, equation (1) yields the temperature dependence of the extraordinary (ordinary) refractivity, $R_\parallel(R_\perp)$, per molecular mass. These results, near the I_{RE}–N_D and N_D–I phase transitions, are shown in figure 5. The ordinary (extraordinary) molar refractivity has a minimum (maximum) near the temperature that the optical birefringence reaches a maximum value (see figure 3), and the difference between $R_\parallel$ and $R_\perp$ near the I_{RE}–N_D

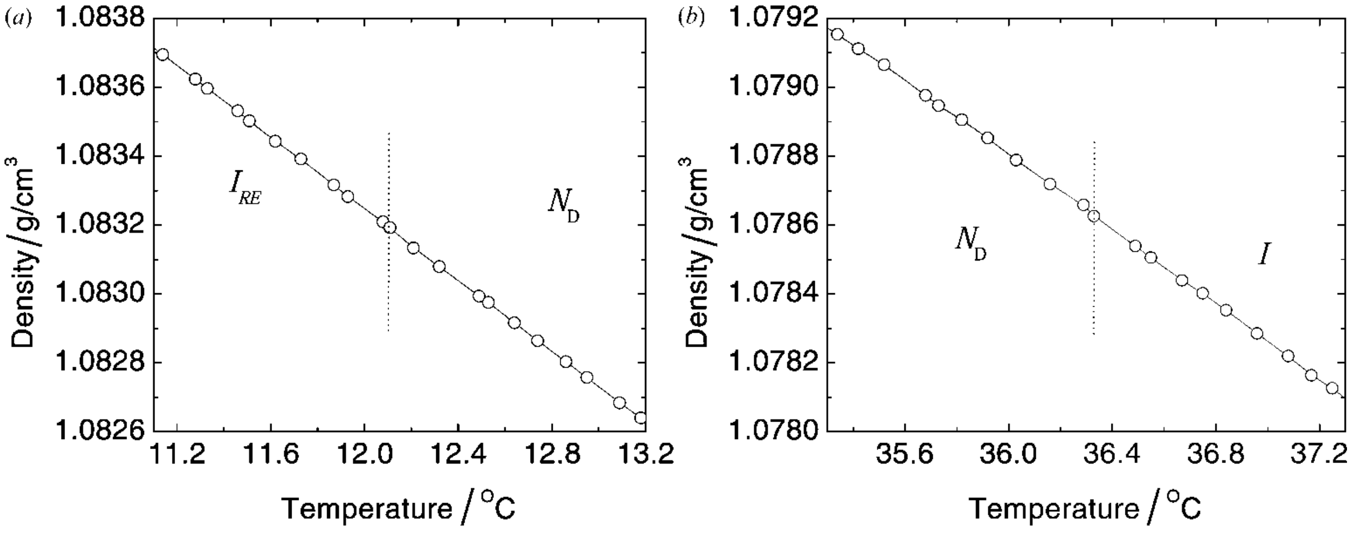

Figure 4. Density vs temperature for the KL system: (*a*) near the I_{RE}–N_D phase transition; (*b*) near the N_D–I phase transition. The solid line is a guide to the eye.

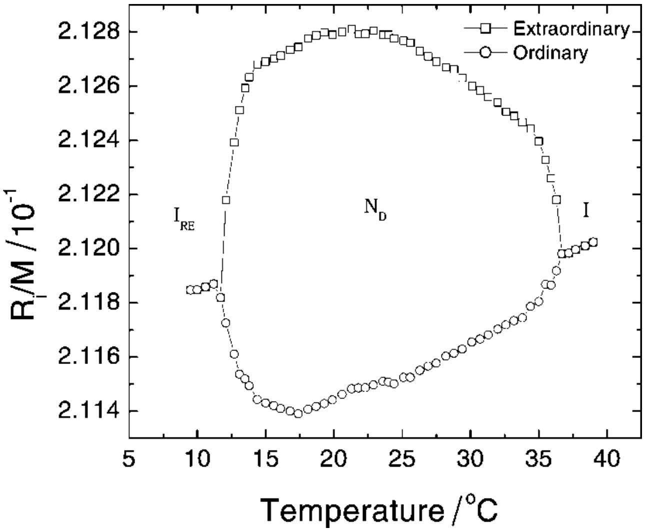

Figure 5. Extraordinary ($R_{\|}$) and ordinary ($R_{\perp}$) molar refractivity per molecular mass vs temperature of the KL system. The solid line is a guide to the eye.

phase transition is greater than that in the vicinity of the N_D–I transition.

It is important to note that the molar refractivity [14] R_i is associated with the mean polarizability α_i of the micelles. Thus, the behaviour of the molar refractivity determined at each phase transition by our experimental data may be attributed to structural changes in the micellar configuration at the transitions. In fact, this result is consistent with X-ray diffraction experiments showing a micellar shape change near the I_{RE}–N_D and N_D–I phase transitions in a similar lyotropic mixture [12]. From a theoretical point of view, this reentrant isotropic–discotic nematic phase transition has been attributed to the temperature-dependent interaction associated with the thermal variation in the shape anisotropy of the micelles [18]. Furthermore, the study of the order parameter using mean-field theory [19] in the vicinity of these phase transitions could now be of considerable interest, given our experimental results.

In summary, we have performed a refractive index study near the I_{RE}–N_D and N_D–I phase transitions of a lyotropic discotic nematic phase. The experimental results agree with the phase diagram proposed by Yu and Saupe [3] and confirm the existence of the reentrant isotropic phase. The transitions are marked by changes in the temperature dependence of the molar refractivity, indicating that a possible variation of the micellar structures takes place at the phase transitions [20]. Experiments concerning the biaxial nematic phase (N_B) are more critical, since this phase has three refractive indices.

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