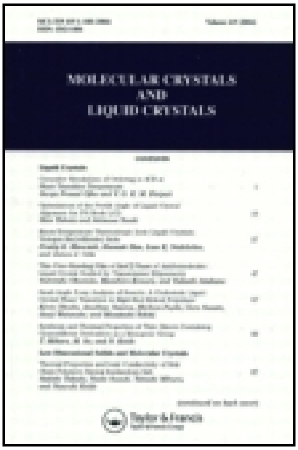

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Molar Refractivity and Thermal Expansion Coefficient of a Lyotropic Nematic Phase

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To cite this article: P. A. Santoro, H. L. F. da Luz & A. J. Palangana (2005): Molar Refractivity and Thermal Expansion Coefficient of a Lyotropic Nematic Phase, Molecular Crystals and Liquid Crystals, 434:1, 291/[619]-296/[624]

To link to this article: http://dx.doi.org/10.1080/15421400590954489

Mol. Cryst. Liq. Cryst., Vol. 434, pp. 291/[619]–296/[624], 2005
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400590954489

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Measurements of the extraordinary/ordinary molar refractivity and thermal expansion coefficient as a function of temperature are presented for the lyotropic mixture of potassium laurate, decanol and water. The measurements cover the range of the calamitic nematic phase (N_C) and the vicinity of the reentrant isotropic (I_{RE})–N_C–isotropic (I) phase transitions. Thermal expansion coefficient (β) was obtained from density data while that the refractivity parameters were determined through of the Vuks's equation together with refractive indices and density values. These parameters are discussed in terms of structural changes in the micellar configuration at the phase transitions.

Keywords: calamitic nematic; isotropic reentrant; molar refractivity; thermal expansion coefficient

INTRODUCTION

In the temperature region of phase transition of liquid crystals anomalies in the thermodynamic properties and macroscopic order parameters are to be expected [1,2]. There are thermodynamic parameters, such as thermal expansion coefficient (β), that depends on both structure and spatial rearrangements of building blocks of the material. Optical anisotropy ($\Delta n = n_e - n_o$) can yields information about the particles (molecules) because refractive index (n) is a property that arises from interaction of

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

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eletromagnetic waves and electrical charges that are present in micelles. In this way, these two parameters can be useful to understand the changes that occurs in the phase transitions of liquid crystals.

Lyotropic uniaxial nematic phases are known as calamitic (N_C) and discotic (N_D), depending on their optical and diamagnetic anisotropy [3–6]. The N_C (N_D) phase presents negative (positive) optical birefringence (Δn) and positive (negative) diamagnetic anisotropy (χ_a). The ternary system potassium laurate (KL), decanol (DeOH) and D_2O is capable of forming both uniaxial nematic phases, each of them limited by two isotropic phases: one reentrant isotropic phase that takes place at lower temperature and another isotropic phase in high temperature [6]. In this system, the biaxial nematic phase (N_B) was observed [6] between the N_D and N_C phases. However, the stability of this lyotropic biaxial nematic have been questioned [7]. A phase sequence important of this lyotropic system, reentrant isotropic (I_{RE})–calamitic nematic (N_C)–isotropic (I), was recently studied through of the extraordinary and ordinary refractive index measurements using the refractometry technique [8]. This phase sequence is now investigated by means of the extraordinary/ordinary molar refractivity and thermal expansion coefficient behavior as a function of the temperature. These parameters are related with changes in the structures of the micelles at phase transitions.

EXPERIMENTAL

The lyotropic mixture investigated in this work [8] was prepared with the following concentrations in weigth percent: potassium laurate (KL: 29.4), decanol (DeOH:6.6) and water (64.0). The phase sequence were determined by optical microscopy and conoscopic observations, which have shown that it is I_{RE} up to 11°C, being that N_C phase upon heating changes to the isotropic phase at 47°C. The thermal expansion coefficient β as a function of temperature was obtained from density data, near the $I_{RE}-N_C$ and N_C-I phase transitions. Density measurements [9] were determined through the oscillation period by means of an Anton Paar instrument consisting of a microcell (DMA-602HT) and a processing unit (DMA-60). The sample temperature, controlled by a Heto CBN 18–30/HMT 200 circulating temperature bath, were stable to ± 0.01 K. We have used a software and computer to record the densitometer readings and the temperature at the glass housing of the U-tube. Each recorded value of temperature and respective density is an average of three readings, obtained after temperature stabilization. The densitometer was calibrated with water and with air.

RESULTS AND DISCUSSION

Figure 1 and Figure 2 shows the new density experimental data [10], as a function of temperature, near the $I_{RE}-N_C$ and N_C-I phase transitions, respectively. Away from the transition region the density values decreases almost linearly with temperature increases. One can see that near the $I_{RE}-N_C$ transition the density variation is slightly different of, and more pronounced than, the one observed in the N_C-I transition. The inset of Figure (1) and Figure (2) shows the thermal expansion coefficient (β) behavior obtained through the numerical derivative of the density values, $\beta = -1/\rho(\partial p/\partial T)_P$. Note that β presents a well defined peak at the N_C-I transition while this peak practically disappears (is very subtle) at the $I_{RE}-N_C$ transition. This experimental result reflects changes in the structures of the micellar configuration at the transitions [11]. The data indicates yet, from thermodynamic point of view, that the $I_{RE}-N_C$ transition is very weakly a first order phase transition. In this way, using the Vuks's equation it can be shown that the molar refractivity (R_i) can be written as [12]

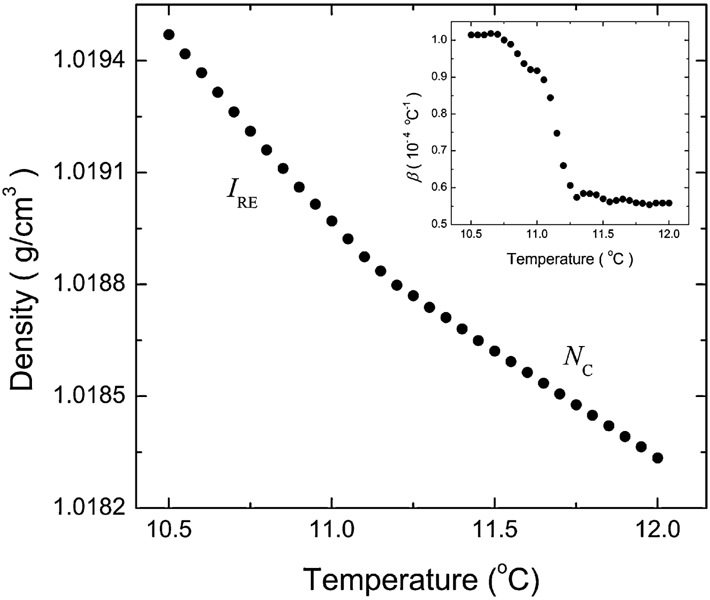

FIGURE 1 Density as a function of temperature near the isotropic reentrant (I_{RE})–calamitic nematic (N_C) phase transition. The inset shows the thermal expansion coefficient vs temperature near the $I_{RE}-N_C$ phase transition.

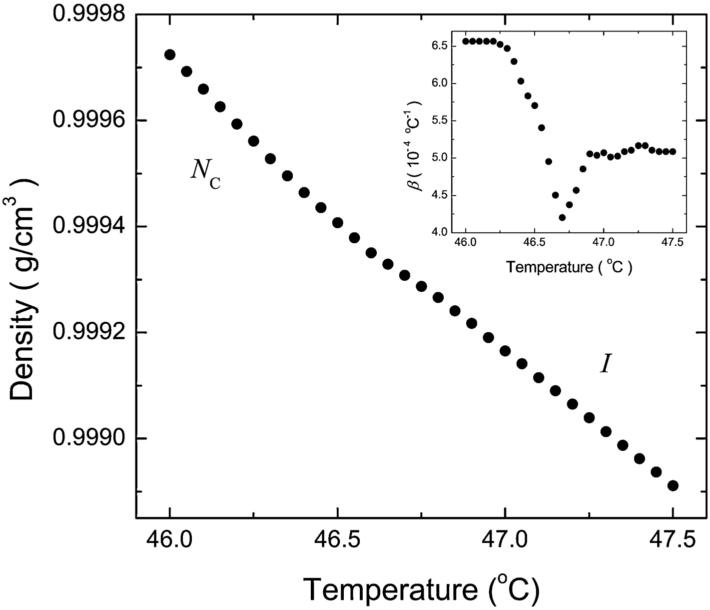

FIGURE 2 Density as a function of temperature near the calamitic nematic (N_C)−isotropic (I) phase transition. The inset shows the thermal expansion coefficient vs temperature near the $N_C - I$ phase transition.

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

where n_i is the $n_{\|(\perp)}$ extraordinary (ordinary) refractive index, $\langle n^2\rangle = \left(n_\|^2 + 2n_\perp^2\right)/3$ is the average value of the refractive index in the calamitic nematic phase, M is the molecular mass and ρ the density. Taking into account the refractive index measurements obtained from Ref. [10] $(n_i^2, \langle n^2\rangle)$ and density values (ρ) obtained here, Eq. (1) yields the temperature dependence of the extraordinary/ordinary refractivity, $R_\|(R_\perp)$, per molecular mass. This result, near the $I_{RE} - N_C$ and $NC - I$ phase transitions and in the range of the N_C phase is exhibited in Figure 3. Note that, $R_\perp\left(R_\|\right)$ has a maximum (minimum) near the temperature where the optical birefringence (Δn) reaches a maximum absolute value as shown in Figure 3 of Ref. [10]. The difference between $R_\|$ and $R_\perp$ in absolute value near the $I_{\mathrm{RE}} - N_{\mathrm{C}}$ transition is greater than that in the vicinity of the $N_C - I$ transition. In this sense, our present experimental results, the thermodynamic (β) and microscopic (R_i) parameters, indicates changes in the structures of the micelles at the $I_{RE} - N_C$ and $N_C - I$ phase transitions. A similar

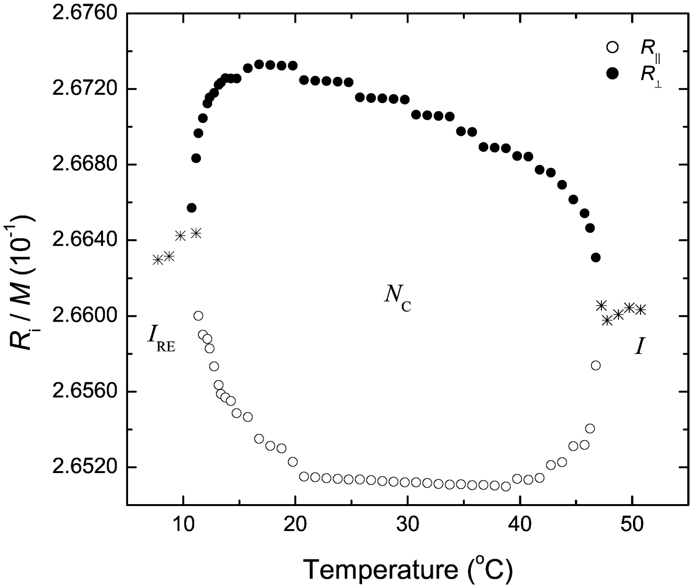

FIGURE 3 Extraordinary ($R_{\|}$) and ordinary ($R_{\perp}$) molar refractivity per molecular mass vs temperature. I_{RE}, N_{C} and I are the isotropic reentrant, calamitic nematic and isotropic phases, respectively.

result [13] was recently determined, using the same technique in a similar lyotropic mixture, near the $I_{\mathrm{RE}}-$ discotic nematic (N_D) and N_D-I phase transitions. Our data when compared with the Figure 5 of Ref. [13] presents an inversion by symmetry in the behavior of the molar refractivity. The anisotropy ($\Delta R = R_{\|} - R_{\perp}$) is negative in the calamitic nematic phase studied here and positive in the discotic nematic phase [13] in accordance with the signal of the optical birefringence (Δn). This accordance between the signals of anisotropy (ΔR) and birefringence is easily verified when we use the optical anisotropy, given by $\Delta n = n_{\|} - n_{\perp}$, and Eq. (1) to obtain $\Delta R = R_{\|} - R_{\perp} = \xi(n_{\|}^2 - n_{\perp}^2)$, where $\xi = M/\rho\left(\langle n^2 \rangle + 2\right)$.

It is interesting to note that, while the thermodynamic parameter behavior (thermal expansion coefficient, β) indicates that the $I_{RE}-N_C$ transition is very weakly a first order phase transition, the optical parameter (anisotropy ΔR) near this transition is greater than that in the vicinity of N_C-I phase transition. A possible explanation for this is that the molar refractivity parameter R_i [14] is related with the mean polarizability α_i of the micelles, being that this latter parameter depends on temperature and micellar shape anisotropy.

Summing up, we have carried out density/thermal expansion coefficient and molar refractivity studies near the $I_{RE}-N_C$ and N_C-I phase transitions of a lyotropic calamitic nematic phase. The existence of the reentrant isotropic phase that takes place at lower temperature in this lyotropic system has been attributed, from theoretical point of view, to the thermal variation in the shape anisotropy [15] of the micelles. The experimental results are compatible with this fact and show that the microscopic optical parameter (molar refractivity, R_i) indicates more clearly the occurence of these changes in micellar configuration. Finally, we mention that critical exponent study [16] in this phase sequence was recently published.

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