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## Coefficient of Electronic Polarizability in a Lyotropic Nematic Phase

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The coefficient of electronic polarizability ( $\phi_i$ ) is determined by means of the density and extraordinary/ordinary refractive indexes measurements 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. These parameters were related to the extraordinary/ordinary refractive indexes via the temperature derivative of the Vuks's equation. The results showed that near the  $I_{RE} - N_C$  and  $N_C - I$  phase transitions the measured value of  $\phi_i$  was found to be about two order of magnitude smaller than that obtained for nematic MBBA system. Sign inversion of this coefficient near these phase transitions is also discussed.

**Keywords:** density; refractive index; coefficient of electronic polarizability.

### INTRODUCTION

Lyotropic liquid crystals (LC) are formed by mixtures of amphiphilic molecules and a solvent (usually water), under convenient temperature and concentration conditions<sup>[1]</sup>. The basic units of these systems are anisotropic micelles<sup>[2]</sup>. In the temperature-concentration phase diagram, two uniaxial and

one biaxial nematic phases have been observed<sup>[3]</sup>. 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<sup>[2]</sup>. Density ( $\rho$ ) and extraordinary ( $n_{\parallel}$ ) and ordinary ( $n_{\perp}$ ) refractive indexes measurements as a function of temperature are very important parameters to study the phase transitions in liquid crystals. These parameters can be related, via the temperature derivative of the Vuks's equation, with the coefficient<sup>[4,5]</sup> of the electronic polarizability ( $\phi_i$ ). 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  $\phi_i$  value is relevant since it provides information about the non-linear optical response of these systems. In this paper, the coefficient  $\phi_i$  is determined as a function of the temperature, in a lyotropic mixture of potassium laurate, decanol and water near the reentrant isotropic-calamitic nematic and calamitic nematic-isotropic phase transitions, using the densitometry and refractometry techniques.

## EXPERIMENTAL

The Vuks's equation relates the microscopic structures of liquid crystal molecules to the refractive indexes as follow<sup>[5-7]</sup>:

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

where  $n_i$  stands for  $n_{\parallel}$  and  $n_{\perp}$ , the extraordinary and the 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.

The parameter  $\phi_i$  can be obtained by differentiating Eq.(1) with respect to the temperature<sup>[8]</sup>:

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

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. Eq.(2) will be used in the sequence to determine the coefficient  $\phi_i$  of a lyotropic mixture of potassium laurate, decanol and water near the reentrant isotropic-calamitic nematic and calamitic nematic-isotropic phase transitions. 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 sequence, determined by optical microscopy and conoscopic observations, is reentrant isotropic (11.0°C)  $\rightarrow$  calamitic nematic (47.0°C)  $\rightarrow$  isotropic. Density measurements<sup>[9]</sup>, near the  $I_{RE} - N_C$  and  $N_C - I$  phase transitions, were determined

through the oscillation period of a *U*-tube (with internal diameter of 2 mm) by means of an Anton Paar instrument consisting of a microcell (*DMA-602HT*) and a processing unit (*DMA-60*). The precision of the densimeter is  $5 \times 10^{-6}$  g/cm<sup>3</sup>. The sample temperature was controlled by a Heto *CB8-30E/DT-1* circulating temperature bath, ensuring that the temperature readings were stable at 0.01K. Special care was taken during the filling procedure to avoid air and air bubbles from getting trapped in *U*-tube. The curved part of the sample tube was electronically stimulated in an undamped harmonic fashion and the direction of oscillation was perpendicular to the plane of the *U*-shaped sample tube.

## RESULTS AND DISCUSSION

The density data as a function of temperature for sample on heating are presented in Figure 1. The experimental results show that the temperature range of the phase transition<sup>[10]</sup> in our sample is of the order 1°C. It can be observed that the density decreases as the temperature increases. An additional change in the density values can be observed around 11.0°C and 47.0°C where the  $I_{RE} - N_C$  and  $N_C - I$  phase transitions occurs, respectively. It's clear from Fig. 1 that the trend of the density values is different between these phase transitions. This behavior of the density indicates a possible change in the shape anisotropy<sup>[11]</sup> of the micelles at each phase transition.

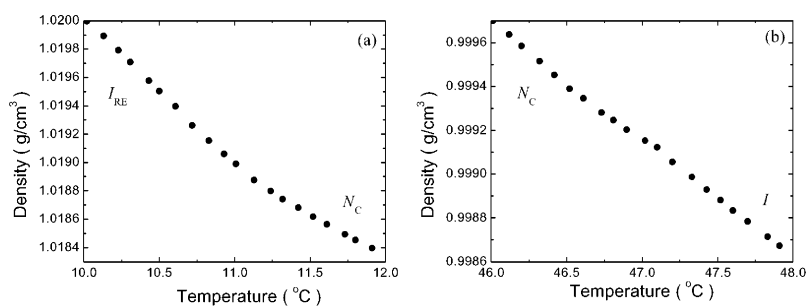


FIGURE 1: Density as a function of temperature in the *KL* system: (a) near the reentrant isotropic-calamitic nematic phase transition; (b) near the calamitic nematic-isotropic phase transition.

Extraordinary ( $n_{||}$ ) and ordinary ( $n_{\perp}$ ) refractive indexes measurements<sup>[12]</sup> as a function of temperature, near of these phase transitions, were performed through Abbe refractometer and are presented in Figure 2. A similar behavior of these parameters was also recently observed in another lyotropic mixture<sup>[13]</sup>, near of the calamitic nematic-isotropic phase transition. Also from Fig. 2 one sees that the reentrant isotropic-calamitic nematic phase is verified by our experimental results.

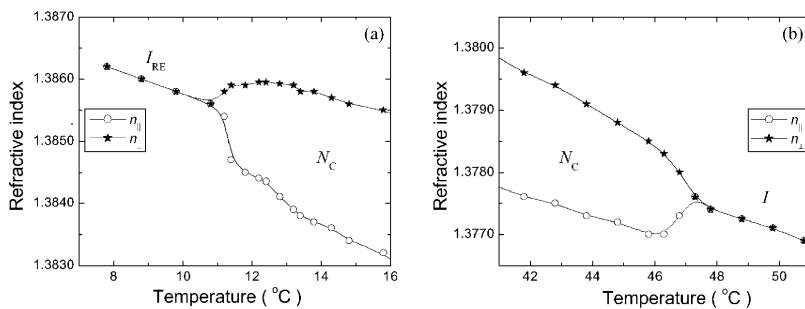


FIGURE 2: Extraordinary and ordinary refractive indexes<sup>[12]</sup> vs temperature in the KL system, for  $\lambda=589.3$  nm: (a) at reentrant isotropic-calamitic nematic phase transition; (b) at calamitic nematic-isotropic phase transition.

The thermal expansion coefficient  $\beta = -(1/\rho)(\partial\rho/\partial T)_p$  as a function of temperature can be obtained from density data, near of these phase transitions. From these experimental results (density/thermal expansion coefficient and extraordinary and ordinary refractive indexes/their respective temperature derivative  $dn_{\parallel}(n_{\perp})/dT$ ), the Eq.(2) yields the temperature dependence of the coefficient of electronic polarizability  $\phi_i$ , near the  $I_{RE} - N_C$  and  $N_C - I$  phase transitions. This result is shown in Figure 3.

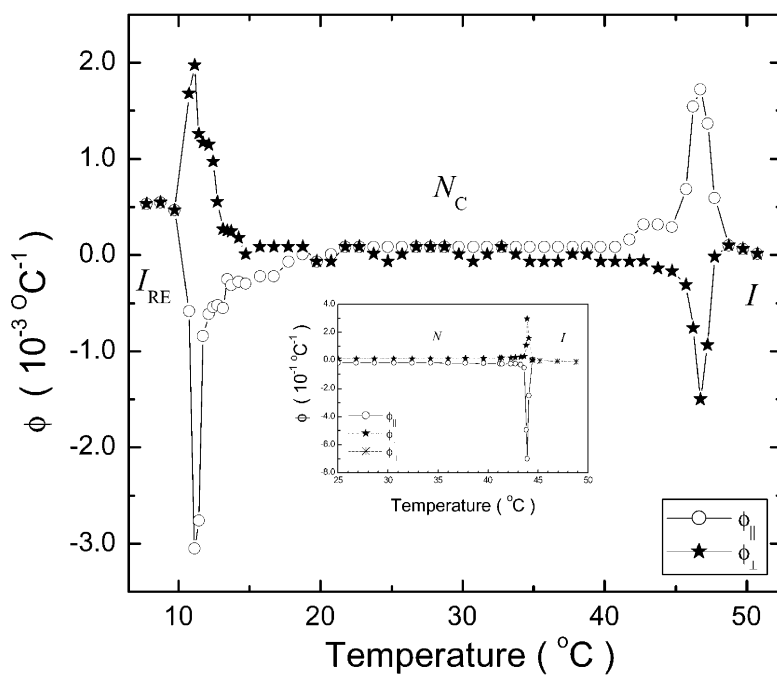


FIGURE 3: Coefficient of the electronic polarizability vs temperature in the *KL* system. The inset shows the coefficient of the electronic polarizability vs temperature at nematic-isotropic phase transition for MBBA system<sup>[14]</sup>.



Let us now consider Eq.(2) in which all the parameters are positive, except  $dn_i/dT$ , which can be either positive or negative. Therefore, the occurrence of the sign change in  $\phi_i$  from positive to negative, is related to  $dn_i/dT$ . As one can see from Fig. 3, the extraordinary coefficient of the electronic polarizability ( $\phi_{\parallel}$ ) changes of sign (from positive to negative) at the  $I_{RE} - N_C$  phase transition. However, for the homeotropic geometry, the sign of ordinary coefficient ( $\phi_{\perp}$ ) does not change in this phase transition. On the other hand, near the  $N_C - I$  phase transition, the ordinary coefficient  $\phi_{\perp}$  change of sign, while  $\phi_{\parallel}$  does not change of sign remaining with a positive value. It was recently reported that in another lyotropic mixture the coefficient  $\phi_{\perp}$  has a similar behavior<sup>[14]</sup>. This sign change of the extraordinary (ordinary) coefficient observed near the  $I_{RE} - N_C$  ( $N_C - I$ ) phase transition can be connected to some type of change in the micellar structure.

For the planar (homeotropic) geometry, one can note a well defined peak in the values at the  $I_{RE} - N_C$  and  $N_C - I$  phase transitions, where in absolute values  $\phi_{\parallel} > \phi_{\perp}$ . This increase in the  $\phi_{\parallel}$  values in the long axis of the micelles, near these phase transitions, 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. The inset in Figure 3 shows the extraordinary and ordinary coefficient vs temperature, recently determined for MBBA system<sup>[14]</sup>. We can observe that the order of magnitude of  $\phi_i$  in nematic thermotropic is about two times larger than in

nematic lyotropic. This experimental result shows an important difference between the two uniaxial nematic lyotropic and thermotropic liquid crystals studied here, in terms of the strength of their molecular electronic polarizability. We think that for exploring this lyotropic mixture in technological devices may be necessary to improve its optical and orientational properties by doping the nematic sample with ferrofluid.

In summary, we have obtained via Vuks's equation, the temperature dependence of the coefficient of electronic polarizability of a lyotropic mixture near the reentrant isotropic-calamitic nematic and calamitic nematic-isotropic phase transitions. This coefficient reveal the strength of the molecular polarizability of this system. We have shown that the order of magnitude of  $\phi_i$  in nematic lyotropic is two times smaller than nematic thermotropic. Our results also indicate that in absolute values,  $\phi_{\parallel} > \phi_{\perp}$  for both lyotropic phase transitions studied in this work. Additional experiments in lyotropic ferronematic and near the reentrant isotropic-discotic nematic and discotic nematic-isotropic phase transitions are in progress.

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