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## Liquid Crystals

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# Reentrant isotropic – discotic nematic phase transition: a critical exponent study

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In this work the critical exponents associated with the behavior of the macroscopic orientational order parameter are determined near the reentrant isotropic ( $I_{RE}$ )–discotic nematic ( $N_D$ ) and  $N_D$ –isotropic (I) phase transitions in a lyotropic mixture of potassium laurate, decanol and  $D_2O$  by measurement of optical birefringence. The critical exponents found indicate that the low temperature  $N_D$ – $I_{RE}$  phase transition is quasi-continuous, having a critical exponent,  $\beta_1 \sim 0.17$ , which is markedly different from that found at the classical  $N_D$ –I phase transition,  $\beta_2 \sim 0.38$ . The results are discussed and compared with others obtained with different lyotropic mixtures.

## 1. Introduction

Through the years, the multiplicity of phases found in liquid crystal materials has astonished researchers [1]. The physical richness of these materials makes them ideal for the study of phase transitions: they exhibit continuous and non-continuous phase transitions and even apparent contradictory behavior may be observed in the sequence of their phases. For example, in the so-called reentrant phases, thermodynamic phases apparently more symmetric are created as the temperature is reduced, suggesting the violation of one of the basic laws of nature: that a decrease in temperature should be followed by a decrease in entropy, not by an increase. The pioneering work of Cladis [2], using a mixture of HBAB and CBOOA, showed that a smectic A phase can revert to a nematic phase with the reduction of temperature, and *vice versa*. Since then, further examples of such unexpected behavior have been reported. In the history of the lyotropic materials, the work of Yu and Saupe [3] became a landmark. Using the lyotropic mixture potassium laurate (KL)/decanol (DeOH)/ $D_2O$ , they discovered the biaxial phase and, in addition, found a nematic phase bordered by two isotropic phases—the usual isotropic phase when the temperature was increased, and a remarkable reentrant isotropic phase when the temperature was reduced.

In this context, some microscopic models have been introduced to explain this unexpected behavior [4, 5]. Today, it seems well established that the mechanism responsible for the reentrant phases is the change in shape of the lyotropic micelles [6–8]. With the reduction of temperature the micellar shape loses its anisotropy, until there insufficient is to sustain an orientated state. The main aim of this work is to perform an experimental study of the critical exponents associated with these transitions when the micelles of the lyotropic mixture have discotic shape. If the change of shape is the mechanism responsible for the occurrence of reentrant phases, there is no reason to believe that such phase transition would have the same thermodynamic properties as observed at high temperatures.

## 2. Fundamentals

The loss of orientational order through the Brownian rotational vibration of the anisotropic micelle is the mechanism driving the high temperature, and classical, nematic–isotropic (N–I) phase transition [9]. Otherwise, at the nematic–reentrant isotropic (N– $I_{RE}$ ) phase transition it is the micellar anisotropy that is lost. So there is no reason to believe that these two phase transitions are exactly the same. A set of experimental data has suggested that the critical exponents associated with the order of these two phase transitions (continuous or non-continuous) are not the same. To our

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knowledge, the first observation concerning the nature of the discontinuity associated with the N–I<sub>RE</sub> phase transition was made by McClymer, Oxborrow and Keyes [10]. They have found that for this transition the associated extrapolated temperature assumes a so small value that the transition in the lower isotropic phase comes much closer to being second order. As the existence (or non-existence) of a discontinuity at a phase transition may reflect the discontinuity (or continuity) of the symmetries of the phases under transformation, the fact that N–I<sub>RE</sub> phase transition is continuous (or very close to it) reveals that the symmetries of the reentrant isotropic and nematic phases are interchangeable without abrupt energy changes [9]. Interestingly enough, this is not observed at the classical N–I transition where, even when presenting a small latent heat, the transition occurs with a clear discontinuity. Moreover, recently it has been shown that for calamitic nematic (N<sub>C</sub>)–I<sub>RE</sub> and N<sub>C</sub>–I transitions the critical exponents associated with the temperature dependence of the order parameter is markedly different when these two phase transitions are compared [11]. In particular, when it is assumed that around the critical points the order parameter has a behavior of the form

$$S_2 = a(|T - T_c|)^\beta \quad (1)$$

it is found that around the N<sub>C</sub>–I<sub>RE</sub> phase transition the exponent  $\beta$  assumes the value  $\beta_1 = 0.16 \pm 0.01$ , while around the N<sub>C</sub>–I transition, it assumes the value  $\beta_2 = 0.36 \pm 0.06$ . As these differences, in the order and the associated critical exponents of the phase transitions, are clearly related to differences in their microscopic nature and, moreover, the N<sub>C</sub>–I<sub>RE</sub> phase transition is associated with the change in shape of the micellar structure, it becomes very relevant to study the values of these physical quantities when the change in shape does not involve calamitic structures, but discotic ones. If the obtained results agree with the previous result, we would conclude that they would be characteristic of the N–I<sub>RE</sub> transition, not being a particular result. This work reports measurements that point to this conclusion.

### 3. Results and discussion

The details of the experimental procedure used to obtain the data that will be analysed in this work have been published previously [12], and only a resume is presented here. The lyotropic mixture was prepared with the following concentrations in weight percent: potassium laurate (KL:24.80), decanol (DeOH:6.24) and deuterium oxide (D<sub>2</sub>O:68.96). The phase sequence,

determined by optical measurements, is reentrant isotropic (I<sub>RE</sub>) up to 12.1°C, discotic nematic (N<sub>D</sub>) from 12.1 to 36.3°C, and isotropic (I) again, above 36.3°C. Extraordinary and ordinary refractive index measurements were performed through an Abbe refractometer (Atago-3T) with an accuracy of  $2 \times 10^{-4}$ , and sample temperature control was stable within 0.01 K. The procedure for refractive index measurements is based on the internal reflection of light at an interface between the nematic sample and the surface of an optical glass prism. An optical polarizer was coupled to the Abbe refractometer to obtain the extraordinary and ordinary refractive index measurements. Figure 1 shows the extraordinary ( $n_{\parallel}$ ) and ordinary ( $n_{\perp}$ ) refractive indices versus temperature in the range of the N<sub>D</sub> phase, including the N<sub>D</sub>–I<sub>RE</sub> and N<sub>D</sub>–I phase transition regions. From the extraordinary and ordinary refractive indices one obtains the optical birefringence,  $\Delta n = n_{\parallel} - n_{\perp}$ , which is positive in this discotic nematic phase and negative in the calamitic nematic phase [13].

The optical birefringence  $\Delta n$  provides a macroscopic measurement of the uniaxial anisotropy of the sample and it can be taken as a measure of the order parameter  $S_2$  [1]. That is,  $\Delta n = \eta S_2$ , where  $\eta$  is a normalization constant chosen in such a manner that the maximum of  $S_2$  corresponds to  $\Delta n = 1$ ; since, save for a change of scale, the profile of  $S_2$  coincides with that of  $\Delta n$ . A reduced temperature scale,  $t$ , has been built in such a way that the temperature of the N<sub>D</sub>–I<sub>RE</sub> phase transition corresponds to the re-scaled temperature  $t = 0$ , whereas the temperature of the N<sub>D</sub>–I transition

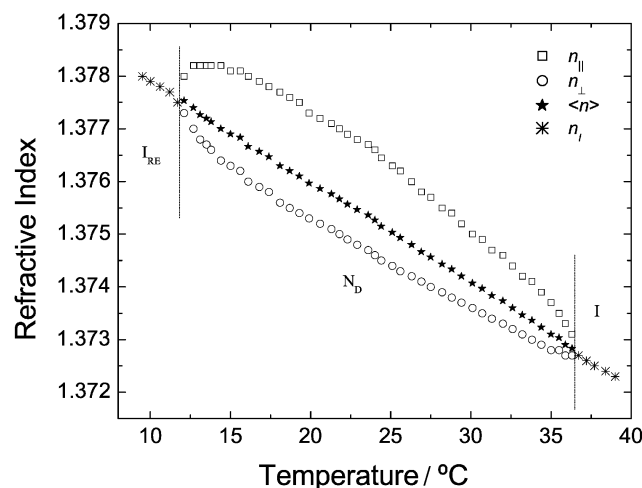


Figure 1. Extraordinary ( $n_{\parallel}$ ) and ordinary ( $n_{\perp}$ ) refractive indices versus temperature [12] of the potassium laurate/decanol/D<sub>2</sub>O mixture, for sodium D line ( $\lambda = 589.3$  nm).  $\langle n \rangle$  is the mean value of the refractive index; I<sub>RE</sub>, N<sub>D</sub> and I are the isotropic reentrant, discotic nematic and isotropic phases, respectively.

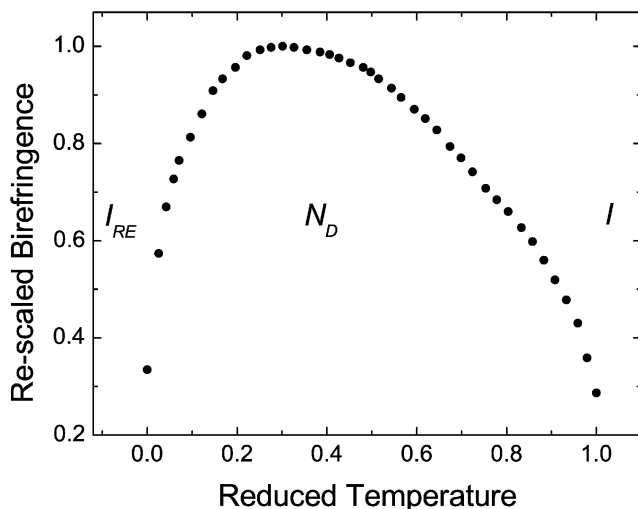


Figure 2. Re-scaled birefringence versus reduced temperature in the discotic nematic phase range, obtained from  $\Delta n = n_y - n_{\perp}$  from figure 1. According to the basis of liquid crystal theory [1] the order parameter would be proportional to  $\Delta n$ . In this sense, the different slope of this curve around the critical points indicates that the critical exponents associated with the order parameter at these two phase transitions are not

corresponds to  $t=1$ , as shown in figure 2. In this case, we have two critical points, at  $t_{N_D I_{RE}} = 0 - \varepsilon_1$  and  $t_{N_D I} = 1 + \varepsilon_2$ , where  $\varepsilon_1$  and  $\varepsilon_2$  are small parameters that give the extrapolated temperature positions where the order parameter would reach the value  $S_2 = 0$ . Of course, when it is found that one of them (or both) is different from zero,  $\varepsilon_i \neq 0$ , for  $i=1$  or  $i=2$ , a first order phase transition occurs. Otherwise, one would have a second order phase transition [9, 14].

So, it can be assumed [11] that around each isolated transition point  $T_c$  we would have  $\Delta n = \alpha(|T - T_c|)^{\beta}$ , from which follows that  $\ln(\Delta n) = \ln(\alpha) + \beta \ln(|T - T_c|)$ . Consequently, around each critical point

$$\beta = \frac{\partial \ln(\Delta n)}{\partial \ln(|T - T_c|)}.$$

One can note that this logarithmic derivative of  $\Delta n$  with respect to the logarithm of  $|T - T_c|$  excludes any dependence of the results on  $\alpha$  (or  $\eta$ ).

Hence, in the graphs of the experimental data of  $\ln(\Delta n)$  as a function of the values of  $\ln(|T - T_c|)$ , the value of the slope of the resulting curve, at the region of  $T_c$ , would correspond to the value of the corresponding critical exponent. Explicitly:

$$\begin{aligned} \beta_1 &= \frac{\partial \ln(\Delta n_{N_D I_{RE}})}{\partial \ln(t - t_{N_D I_{RE}})} \\ \beta_2 &= \frac{\partial \ln(\Delta n_{N_D I})}{\partial \ln(t_{N_D I} - t)} \end{aligned} \quad (2)$$

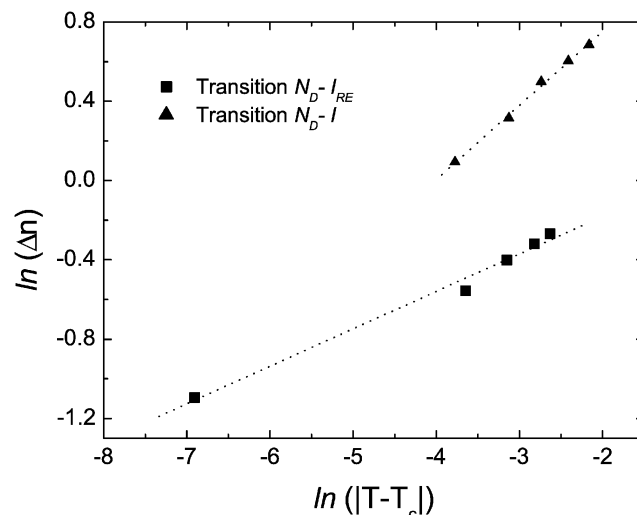


Figure 3. Birefringence data points plotted as  $\ln(\Delta n)$  as a function of  $\ln(|T - T_c|)$ , for  $T_c = T_{N_D I_{RE}}$  (squares) and for  $T_c = T_{N_D I}$  (triangles). Because in this scale these points become distributed as a straight line, the computation of  $\beta$  from equation (2) becomes immediate; that is, the slope of this curve would correspond, at the region of the critical point, to the critical exponent.

The best fits that we have found are shown in figure 3: they are given by  $t_{N_D I_{RE}} = 0.00$ , and by  $t_{N_D I} = 1$ , that is  $\varepsilon_1 = 0.01$  and  $\varepsilon_2 = 0.10$ . The mean value of the critical exponents so obtained are  $\beta_1 = 0.18 \pm 0.01$ , and  $\beta_2 = 0.37 \pm 0.01$  at the  $N_D - I_{RE}$  and  $N_D - I$  phase transitions, respectively. This result indicates that  $N_D - I$  is a first order phase transition, with a non-classical critical exponent. Otherwise, as has already been observed [10, 11], the extremely reduced value found for  $\varepsilon_1$  gives a strong indication that  $N_D - I_{RE}$  is a second order phase transition, with a non-classical critical exponent.

Some years ago, in the work that gave the first experimental evidence that the driving force for the  $N_D - I_{RE}$  transition [6] is the micellar shape variation, the similar lyotropic mixture investigated in this work was considered to produce optical birefringence data similar to the data obtained here. We note that the birefringence data of [6] give the same profile as obtained with the data from our measurements; their slopes, around the critical points, show the same dissimilarities found in the measurements presented in figure 2. This is a clear indication that those measurements already indicated the difference in the critical exponents that we have found here. We have worked with the data of [6] and the results obtained for the critical exponents are essentially the same as reported here.

Finally, as a conclusion from our results, we can affirm that, independently of the shape anisotropy of the micelles involved in the experiment (calamitic or discotic), the low temperature  $N_{C(D)} - I_{RE}$  transition has

a very small discontinuity in the order parameter with an associated critical exponent presenting a value that is approximately half of that observed at the classical  $N_{C(D)}$ -I phase transition.

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