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Optical birefringence and its critical behavior in the vicinity of nematic–smectic A phase transition in a binary mixture

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ABSTRACT

Optical birefringence (Δn) measurements as a function of temperature have been performed for binary mixtures of octyloxy cyanobiphenyl (8OCB) and octyl cyanobiphenyl (8CB) liquid crystals by means of a high resolution temperature scanning technique. The temperature dependence of the birefringence (Δn) was determined from the transmitted intensity data for wavelengths $\lambda = 532$ nm. Using a fitting procedure consistent with the mean field theory and the first order nature of nematic–isotropic (N–I) phase transition, the order parameter critical exponent β has been determined. The critical behavior of the nematic–smectic A (N–SmA) phase transition has been investigated from the high resolution birefringence data and the nature of this transition in the mixtures has been assessed. From the evolution of the critical exponent α, it has been possible to predict the limiting value of the McMillan ratio for the tricritical point (TCP) as well as the 3D-*XY* universality class.

1. Introduction

Liquid crystal displays (LCDs) are evolving as the world's dominant mode of information display, rapidly replacing other display media, and are clearly established as one of the top few industrial technologies [1–4]. The development of new liquid crystal (LC) compounds requires innovative and comprehensive knowledge in the entire range of multidisciplinary topics associated with the science and technology of LCDs. Certain organic materials exhibit the liquid crystalline state as an intermediate phase between the solid and the liquid states, also known as mesophases [5]. Liquid crystalline compounds possess many fascinating mesophases. The simplest mesophase is the nematic (N). Within the nematic (N) phase formed by rod-like molecules, a long-range orientational order of the long molecular axis along a preferred direction called the director is maintained, with no long range correlation of the center of mass of the molecules leading to the absence of positional ordering of the molecules. In smectic phases however, in addition to the long-range orientational order, partial positional order is also present. In the smectic A (SmA) phase, of relevance here, a one dimensional layering exists with the layer normal parallel to the director.

In spite of several experimental and theoretical efforts, different aspects of nematic–smectic A (N–SmA) phase transition are not fully understood. The exact nature of the N–SmA phase transition is a matter of controversy owing to the non-universality of the critical exponent describing the transition. Four decades ago on the basis of mean field theory Kobayashi [6] and McMillan [7] had predicted that the nematic–smectic A (N–SmA) phase transition can either be first order or second order depending upon the value of McMillan ratio (T_{NA}/T_{NI}), where T_{NA} and T_{NI} are the nematic–smectic A (N–SmA) and nematic–isotropic (N–I) phase transition temperatures respectively. The N–SmA phase transition is second order in nature when $T_{NA}/T_{NI} < 0.87$ and of first order above this limiting value [7]. The smectic A phase possesses orientational order along with one dimensional positional order which can be considered as a density modulation expressed in terms of a two component complex order parameter. This indicates that the nematic–smectic A phase transition belongs to the 3D-*XY* universality class [8]. In accordance with the earlier predictions, de Gennes showed, on the basis of Landau free energy expansion, that weak coupling (for a wide nematic range) between the nematic and smectic order parameter results in a second order N–SmA transition while strong coupling (for a narrow nematic range) yields a first order transition through the tricritical point (TCP) [8,9]. Different experimental observations reveal that the crossover from second order to first order nature of N–SmA transition is not universal. Although, the theoretical limiting value of the McMillan ratio is 0.87 for the tricritical point (TCP), but

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experimentally it is found to lie in between 0.942 and 0.994 [10–13]. Moreover, Halperin, Lubensky and Ma (HLM) [14] have predicted that the coupling between the nematic director fluctuations and smectic A order parameter makes the N–SmA transition always first order. Therefore, in this case the concept of tricritical point (TCP) is ruled out.

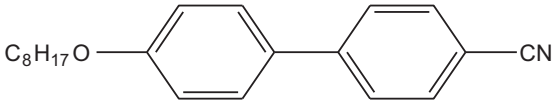
In the present work we have chosen two liquid crystalline compounds 8OCB and 8CB for preparing binary mixtures due to their simple molecular configuration and stability over a large temperature region. These compounds and their mixtures are the good candidates for verifying the general concepts of phase transitions and critical phenomena. We report the optical birefringence (Δn) measurements on the binary system of 8OCB+8CB determined from a high resolution temperature scanning technique. The critical behavior and nature of the N–SmA phase transition have been discussed in detail and the critical exponent (α) for this phase transition has been explored. In addition, the order parameter critical exponent (β) has also been determined from a four parameter expression.

2. Experimental

2.1. Materials

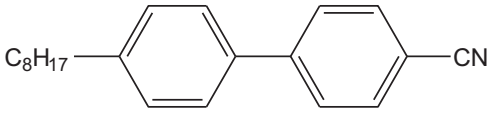
The compounds 8OCB and 8CB were purchased from Merck, U. K. and both were used without further purification. The structural formulae and chemical names of the two liquid crystalline compounds are as follows:

Component 1: Octyloxy cyanobiphenyl (8OCB)



Cr 54.5 °C SmA 67 °C N 80 °C I

Component 2: Octyl cyanobiphenyl (8CB)



Cr 21.5 °C SmA 33.5 °C N 40.5 °C I

Five mixtures have been prepared having molar concentrations of 8OCB equal to 0.155, 0.310, 0.501, 0.753 and 0.850. The nature of the phases and the corresponding phase transition temperatures have been determined by a polarizing optical microscope (Motic BA 300) equipped with a Mettler FP900 hot stage.

2.2. Optical transmission (OT) method

High resolution optical birefringence (Δn) measurements were carried out by measuring the intensity of a laser beam transmitted through a planar aligned LC cell of thickness 5 μm. A solid state green laser ($\lambda=532$ nm) was used to probe its phase retardation. The temperature of the cell was controlled and measured with a temperature controller (Eurotherm PID 2404) with an accuracy of ± 0.1 °C by placing the LC cell in a heater made of brass. The intensity of the transmitted light was measured by a photo-diode at an interval of 3 s. The heater temperature was varied at a rate of 0.5 °C min^{-1}; this translates into a temperature difference of 0.025 °C between two successive readings. The experimental details for the birefringence measurement from the optical transmission method in the nematic and SmA phases have been illustrated in our earlier publications [15,16].

3. Results and discussion

3.1. Phase diagram

The phase diagram for the binary system 8OCB+8CB as obtained from polarizing optical microscopy (POM) studies is shown in Fig. 1. The nematic–isotropic, nematic–smectic and the melting temperatures are plotted against the mole fraction of 8OCB. Phase transition temperatures were recorded during cooling. The complete phase diagram for this binary system was investigated by Sahraoui et al. [17] and later by Sied et al. [18]. All the phase transition temperatures reported here are in close agreement with those reported in the literature. It is observed that the nematic region broadens as the concentration of 8OCB increases.

3.2. Optical birefringence measurements

The optical birefringence (Δn) of the mixtures has been measured by means of a high resolution temperature scanning technique at $\lambda=532$ nm as shown in Fig. 2. The Δn data covers the nematic as well as smectic A phases of the mixtures. Near the nematic–isotropic transition temperature (T_{NI}), Δn changes quite rapidly whereas at the nematic–smectic A transition a sluggish but noticeable change is observed. It is well known that birefringence measurement provides clear information regarding the nature of phase transition and molecular ordering. The higher value of Δn in the smectic phase compared to nematic phase is due to increased ordering, which results in an increase in the optical anisotropy. Near the vicinity of the N–SmA transition, pretransitional evidence for the coupling between the nematic and smectic ordering has clearly been observed for all the mixtures under study.

Recently, a four parameter power-law expression [19], consistent with the mean-field theory for critical as well as tricritical behavior of weakly first-order transition, has been introduced and expressed in the form

$$D = A\left[B + (1-B)\left(1-\frac{T}{T^*}\right)^{\beta}\right] \quad (1)$$

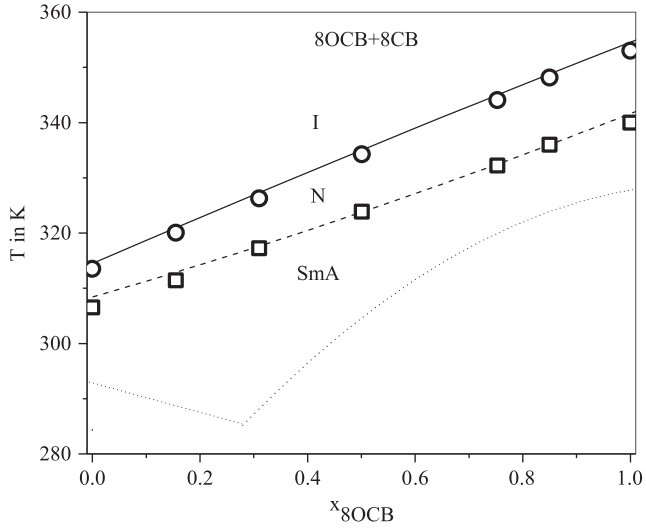


Fig. 1. Phase diagram for the binary system of 8OCB+8CB. x_{8OCB} is the mole fraction of 8OCB. I—isotropic phase, N—nematic phase and SmA—smectic A phase. o —nematic to isotropic phase transition temperature (T_{NI}); □—nematic–smectic A phase transition temperature (T_{NA}). Solid, dashed and dotted line represent the nematic–isotropic, nematic–smectic A phase transition and melting temperatures respectively throughout the entire composition as obtained in Refs. [17,18].