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A simple method to determine high-accuracy refractive indices of liquid crystals and the temperature behavior of the related optical parameters via high-resolution birefringence data

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ABSTRACT

We report new high-resolution experimental data for the optical birefringence over the temperature range spanning the nematic (N) and smectic A (Sm A) phases of various liquid crystals (LCs) by means of a rotating-analyzer method. In this work we proposed a simple procedure to determine high-accuracy extraordinary (n_e) and ordinary (n_o) refractive indices of LCs both in the N and Sm A phases based on the birefringence measurements. We then show that, apart from the birefringence data, the procedure needs only a single value for the refractive index which is the value of that in the isotropic (I) phase just above the N–I transition temperature. The consistency of our approximation has been checked under the framework of the Vuks model using the criteria found in the literature. We then conclude that our proposal is self-consistent for obtaining the extraordinary and ordinary refractive indices of LCs with high accuracy and seems to be readily applied as compared to the other methods reported to date and also that temperature variation of n_e and n_o refractive indices is well portrayed by the fit expression presented here for the first time contrary to the Haller extrapolation method. Furthermore, we then show that, without addressing density measurements, the proposed method allows one to obtain the temperature dependence of normalized molecular polarizabilities for extraordinary and ordinary rays, and the effective geometry parameter α_{eg}. It has been observed that α_{eg} changes linearly with the order parameter and the same slope value has been obtained for all investigated samples, which can be ascribed to the global behavior of the nematic phase, which has been reported most recently.

1. Introduction

Liquid crystalline materials are known to be composed of large asymmetric molecules which melt in stages from the anisotropic crystalline solid to an isotropic liquid state. These materials exhibit a wide variety of ordered phases, differing from each other in their degree of order and symmetry [1,2]. For thermotropic liquid crystals, two of the most extensively studied phases, both experimentally and theoretically, are the orientationally ordered nematic (N) phase and the layered smectic (Sm) phase [1–4]. In the nematic phase the molecules, without any long-range positional order, have only long-range orientational order and they tend to be parallel to some common axis, the so-called director. In addition to the orientational order of nematics, in the smectic A (Sm A) phase, the director is perpendicular to the smectic layer plane, and within the layers there is no long-range positional order [1–3]. Liquid crystals (LCs) have been the subjects of vigorous investigation since they possess many interesting and versatile properties and find applications from display devices [5–7] to beam steering devices and tunable photonics [8]. Thus, the optical characterization of LCs is of great interest from the application point of view. The knowledge of the temperature dependence of the refractive indices, optical anisotropy, molecular polarizabilities and order parameter is crucial due to the fact that the refractive indices and the optical anisotropy characterize the possibilities of LC compounds in the modulation of light.

It is well known that the refractive indices are frequently measured by means of Abbe-type refractometer [9,10] and via wedge [11,12] or thin prism methods [13,14]. Also, the optical birefringence has usually been measured by Newton's rings technique [11,12,15,16]. On the other hand in the abovementioned optical studies [9–16] since the refractive index and birefringence measurements are based on the visual inspection by means of Abbe type refractometer and wedge technique for the former and Newton's rings method for the latter, in most cases the precision in the optical data is unsatisfactory.

Moreover, during recent years, there has been considerable interest in the rate of change of the refractive indices with temperature and the temperature dependence of the effective geometry parameter, defined as the ratio of ordinary and extraordinary refractive indices, [17–19] since the former is related to the so-called crossover temperature, being a crucial parameter for the characterization of LC materials for

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the application point of view in display technology and non-linear optics while the latter is helpful in better understanding of light propagation as argued by several groups [11,20]. Another issue about the optical studies in Refs. [17–20] is the fact that the Haller approximation [21] was used to quantify the temperature variation of the refractive index data. In fact, it has been shown that this extrapolation method yields systematically lower values for the critical exponent β [22–24]. Thus, in order to quantify the optical data, the Haller method is known to be unacceptable and also incompatible with the weakly first-order nature of the nematic–isotropic (N–I) transition [1,4,25].

Due to the fact that accurate values of the birefringence can be determined directly with an interference method [26,27] as compared to measure the refractive indices separately, in this work we propose a simple alternative procedure to determine the temperature dependence of the extraordinary (n_e) and ordinary (n_o) refractive indices based on the high-precision and resolution birefringence measurements. We show that the procedure needs only a single value for refractive index, namely n_I which is the value of the refractive index in the isotropic phase just above the N–I transition temperature T_{NI}, apart from the birefringence. The n_I value can be determined easily by Abbe type refractometer in the isotropic phase. Furthermore, we also pursue this idea determining normalized molecular polarizabilities for the extraordinary and ordinary rays as a function of temperature without addressing density measurements [13,20]. In this work we present new high-resolution experimental data for the temperature variation of the optical birefringence in the N and Sm A phases of various LCs by using a rotating-analyzer method, known to be a very accurate interference technique [28–30]. In recent past, this technique has already proven its particular suitability for the study of the Halperin–Lubensky-Ma (HLM) effect [30,31]. We emphasize here that this method can be successfully applied to both binary mixtures of LCs and LC + non-mesogenic dopants for the experimental test of the HLM effect [32]. Further studies are in progress and will be reported elsewhere.

In recent years, liquid crystalline composites produced by dispersing several distinct nano-scale structures such as carbon nanotubes [33], nanoparticles [34], and quantum dots [35] have gained considerable interest owing to their importance from both fundamental and technological points of view. Thus, it would be challenging to investigate the temperature behavior of the ordinary and extraordinary refractive indices of above-mentioned liquid crystalline composites and systematic studies on this subject are still lacking. In our opinion this simple method is quite useful to extract temperature variation of the ordinary and extraordinary refractive indices of above-mentioned liquid crystalline composites with high precision.

The liquid crystalline materials analyzed here are 4-pentyl-4′-cyanobiphenyl (5CB), 4-octyl-4′-cyanobiphenyl (8CB), 4-heptyloxy-4′-cyanobiphenyl (7OCB), 4-butyloxyphenyl-4′-decyloxybenzoate $\left(\overline{10}.\mathrm{O}.\overline{4}\right)$, and E7 which is a commercial eutectic mixture of alkyl and alkyloxycyanobiphenyls and triphenyls, composed mainly by 5CB (~51 %). In order to validate the procedure that we propose here, we have especially used the above-mentioned materials since one can easily find refractive index data of these LCs in literature [22,36,37].

2. Theoretical considerations

Due to anisotropic nature of LCs, in a homogeneous cell, the LC exhibits two principal refractive indices n_e and n_o for the extraordinary and ordinary rays respectively. n_e and n_o refractive indices can be written in terms of average refractive index $\langle n\rangle = (n_e + 2n_o)/3$ and the optical birefringence $\Delta n = n_e - n_o$ in the form:

$$n_e = \langle n\rangle + \frac{2}{3}\Delta n \tag{1a}$$

$$n_0 = \langle n\rangle - \frac{1}{3}\Delta n. \tag{1b}$$

Noting that $n_e^2 - n_o^2 = 2\overline{n}(\Delta n)$ where $\overline{n} = (n_e + n_o)/2$, we propose here that it is quite reasonable to take that $\overline{n} \approx n_I$ and $\langle n^2\rangle \approx \overline{n}^2 \approx n_I^2$, and also $\langle n\rangle \approx n_I$ with n_I the value of the refractive index in the isotropic phase just above T_{NI}. Since the value of the refractive index of most LCs in the isotropic liquid phase does not change considerably, this approximation seems reasonable.

Vuks [38] suggested a semi-empirical expression that relates the microscopic molecular polarizabilities to refractive indices [9,11]. While discussing the validity of the Vuks approach, Wu et al. [19,39] derived the relations

$$\frac{\langle n\rangle}{\langle n^2\rangle + 2} \approx \frac{\sqrt{2}}{4} \tag{2a}$$

$$\left\langle n^2\right\rangle + 2 \approx \sqrt{10}\langle n\rangle - 0.5 \tag{2b}$$

where $\langle n^2\rangle = (n_e^2 + 2n_o^2)/3$, then they showed that Eqs. (2a) and (2b) were satisfied. Similarly, Kuczynski et al. [15] claimed that the so-called Vuks parameters, defined as,

$$V_1 = \frac{\left\langle n^2\right\rangle - 1}{n_e + n_o} \tag{3a}$$

$$V_2 = \frac{9\left(\left\langle n^2\right\rangle - 1\right)}{\Delta n + 2\sqrt{9\langle n^2\rangle - 2(\Delta n)^2}} \tag{3b}$$

must be temperature independent with good accuracy. Finally Soorya et al. [20] used a semi-empirical relation

$$\frac{\left\langle n^2\right\rangle + 2}{n_e + n_o} \approx 1.4 \tag{4}$$

to test the validity of the Vuks model. In the present work, to corroborate our approach we have checked the validity of Eqs. (2a), (2b), (3a), (3b), and (4) by making the assignments $\langle n^2\rangle \approx n_I^2$ and $\langle n\rangle \approx n_I$ and observed that typical error is in between 0.6 % and 0.8 % [22,36,37] over a 10 K-range. Thus, we conclude that this approximation is entirely excellent due to partial cancelation of the changes resulted from small variations in $\overline{n}$ with temperature T. Consequently, with the help of our assumption Eqs. (1a) and (1b) can be rewritten as

$$n_e = n_I + \frac{2}{3}\Delta n \tag{5a}$$

$$n_0 = n_I - \frac{1}{3}\Delta n. \tag{5b}$$

In order to obtain the temperature variation of n_e and n_o refractive indices, the birefringence, Δn is written in terms of the macroscopic order parameter Q. It is well known fact that, as was first pointed out by de Gennes [1], any anisotropic physical quantity can be a measure of orientational order in the N phase. Thus Q is given by

$$Q(T) = \frac{\Delta n(T)}{\Delta n_0} \tag{6}$$

where Δn_0 is the birefringence at $T = 0$ K. Due to the fact that there is no analytic solution to the quartic equation obtained from the minimization of the Landau–de Gennes free energy [1,25], the temperature