



Optical and texture property studies in a nematic liquid crystal mixture

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Received 19 July 2007, accepted 11 June 2008

Abstract : Optical (using 589 nm light source) and texture (using white light source) studies as a function of temperature have been made of a multicomponent nematogen : E47 in the temperature range 288°K to 343°K. The temperature dependence of refractive indices (n_o, n_e) and the birefringence (Δn) agree closely with those obtained using modified four parameter model. A linear relation is observed between birefringence (Δn) and the order parameter (S). The normalized polarizabilities (α_e/α , α_o/α) and order parameter have been determined at different temperatures. The microscopic order parameter and normalized extraordinary polarizability fall with rise in temperature similar to other nematic mixtures. The transition temperature measured using polarizing microscope and optical studies agree closely, and do not show a sharp transition. This transition temperature range behaviour may be due to different components in the mixture.

Keywords : Optical texture, refractive index, order parameter, normalized polarizabilities, birefringence.

PACS No. : 65.30.

1. Introduction

Liquid crystals (LCs) have been used extensively for direct view and projection displays, [1,2], tunable photonics, and nonlinear optics [3,4]. Most of the LC devices use the electric, thermal, or optical-field induced refractive index change to modulate light. One of the most important characteristics of a liquid crystal, which determines the anisotropy in its physical property is its orientational order. The orientational order is expressed in terms of microscopic order parameter S [5,6]. The value of S lies between 1 (for complete order) and 0 (for complete disorder in an isotropic liquid). The microscopic order parameter S differs from the macroscopic order parameter, which can

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be determined easily using any of the bulk tensorial properties, like electric and magnetic susceptibilities, elastic constants, refractive indices, etc. of the liquid crystal. However, it is possible to obtain the microscopic order parameter (S) from the physical properties by applying suitable corrections for internal field [7–9].

In the present paper we are reporting the results of the measurements of extraordinary refractive index (n_e), ordinary refractive index (n_o) in liquid crystal phase and isotropic refractive index (n_i) in isotropic phase of a liquid crystal sample E47 as a function of temperature, using Abbe refractometer with a monochromatic light source. The multicomponent mixture E47, procured from BDH, England, is identical with E7, and our results at 20°C agree closely with the preliminary data sheet of this sample [10]. From the experimental data we have calculated different useful parameters e.g., birefringence (Δn), normalized polarizabilities (α_e/α , α_o/α) and order parameter S [11]. The experimental data have been linked to the theoretically calculated values. It is observed that this model satisfies the experimental data very well. In addition the modified Vuks equation [12] and semi empirical relationship [13] have been verified.

2. Theory

The classical Clausius-Mossotti equation correlates the dielectric constant (ϵ) of an isotropic medium with its molecular polarizability (α) at low frequencies. Replacing $\epsilon = n^2$, the Lorentz-Lorentz equation correlates the refractive index of an isotropic medium with molecular polarizability in the optical frequencies.

Vuks [14] made a bold assumption that the internal field in a liquid crystal is the same in all directions and gave a semi-empirical equation, correlating the refractive indices with the molecular polarizabilities for anisotropic materials.

$$\frac{n_{e,o}^2 - 1}{\langle n^2 \rangle + 2} = \frac{4\pi}{3} N\alpha_{e,o} \quad (1)$$

In eq. (1), n_e and n_o are refractive indices for the extraordinary ray and ordinary ray respectively, N is the number of molecules per unit volume, $\alpha_{e,o}$ is the molecular polarizability, and $\langle n^2 \rangle$ is defined as

$$\langle n^2 \rangle = \frac{(n_e^2 + 2n_o^2)}{3}$$

or

$$(\langle n^2 \rangle)^{1/2} = \sqrt{\frac{(n_e^2 + 2n_o^2)}{3}} \quad (2)$$

we call $(\langle n^2 \rangle)^{1/2}$ the root mean square (rms) refractive index. Since the sample

alignment is planar, the optical anisotropy (Δn) is given by the difference between n_e and n_o i.e. $\Delta n = n_e - n_o$.

Solving eq. (2), we get,

$$n_o = \left(\langle n^2 \rangle \right)^{1/2} - \left(\frac{1}{3} \right) (\Delta n) \quad (3)$$

or

$$n_e = \left(\langle n^2 \rangle \right)^{1/2} + \left(\frac{2}{3} \right) (\Delta n) \quad (4)$$

Li *et al* [15,16] have described n_e and n_o as a function of $\langle n \rangle$ and Δn .

In theory, both n_e and n_o are functions of wavelength and temperature. Here we focus on the temperature effect. According to our experimental data and also as observed earlier [17], $\left(\langle n^2 \rangle \right)^{1/2}$ is more fundamental in nature and its temperature dependence may be written as,

$$\left[\langle n^2 (T) \rangle \right]^{1/2} = A + BT \quad (5)$$

Eq. (5) has a negative slope. On the other hand, birefringence is dependent on the order parameter S . Based on Haller [18] and Wu [19], the order parameter can be approximated as $S = \left(1 - \frac{T}{T_{NI}} \right)^\beta$. Thus the temperature-dependent birefringence has the following form :

$$\Delta n(T) = (\Delta n)_o \left(1 - \frac{T}{T_{NI}} \right)^\beta \quad (6)$$

In eq. (6), $(\Delta n)_o$ is the liquid crystal birefringence in the crystalline state at $T = 0^\circ\text{K}$, the exponent β is a material constant, and T_{NI} is the transition temperature of the liquid crystal material under investigation. Taking logarithm of eq. (6) and giving linear fit, the values of $(\Delta n)_o$ and β are obtained [20].

In case of liquid crystal mixtures, it is quite difficult to find the molecular weight. Also Madhusudana [21] has shown that 1% error in the measurement of density leads to 11% error in the measurements of $(\alpha_e - \alpha_o)$. Therefore, the concept of normalized polarizability is used here, which eliminates the factor "N" containing both density and molecular weight.

The normalized polarizabilities for extraordinary and ordinary rays are then given by :

$$\frac{\alpha_e}{\langle \alpha \rangle} = \frac{(n_e^2 - 1)}{(\langle n^2 \rangle - 1)} \quad (7)$$

$$\frac{\alpha_n}{\langle \alpha \rangle} = \frac{(n_o^2 - 1)}{(\langle n^2 \rangle - 1)} \quad (8)$$

where $\langle \alpha \rangle$ is the average polarizability of liquid crystal molecule and is defined as

$$\langle \alpha \rangle = \frac{\alpha_e + 2\alpha_o}{3} \quad (9)$$

In order to find the best fit with the experimentally values, we have also calculated the order parameter 'S' using modified theoretical Maier-Saupe model [22] which approximates 'S' as $S = 0.1 + 0.9[1 - 0.99(T/T_{NI})^3]^{1/4}$ [23].

Experimentally the order parameter S can be obtained in a number of ways. Here we calculate the orientational order parameter by using Vuks [14] hypothesis.

$$S \left(\frac{\Delta\alpha}{\alpha} \right) = \frac{(n_e^2 - n_o^2)}{(\langle n^2 \rangle - 1)} \quad (10)$$

where $\Delta\alpha$ is the anisotropy of molecular polarizability.

For obtaining S, procedure of Haller is followed. Factor $\frac{\Delta\alpha}{\alpha}$ is called scaling factor and is determined by plotting $\log \frac{(n_e^2 - n_o^2)}{(\langle n^2 \rangle - 1)}$ as a function of $\log \left[1 - \frac{T}{T_{NI}} \right]$. The plot is a straight line and can be extrapolated to $T = 0^\circ\text{K}$ to get the required scaling factor.

3. Experimental details

In order to conduct optical studies values of n_o and n_e of the mixture were measured using an Abbes refractometer (resolution 0.001) at $\lambda = 5893 \text{ \AA}$. The refractometer was precalibrated by measuring the refractive indices of distilled water and benzene. A stable homogeneous alignment, unaffected by temperature cycling was induced in the present case by coating prism surfaces with a thin film of Polyvinyl Alcohol (concentration 0.75% in water) and rubbing unidirectionally repeatedly. Such a method favoured uniform alignment with nematic director parallel to rubbing direction. The PVA coating does not affect the values of refractive indices [8]. Few drops of liquid crystal sample were allowed to fall on both the prism surfaces and were spread with a spatula and lower prism was clamped to the position. A sodium light source (589 nm) is used for illuminating the sample. A converging lens is placed between the lamp and refractometer. The temperature of the sample in Abbe's refractometer is controlled using circulating water from a constant temperature bath. The temperature regulation was better than

$\pm 0.1^\circ\text{K}$. T_o prevent heat loss, proper insulation is made at various points. To measure the temperature of liquid crystal sample a pre-calibrated copper-constant thermocouple is placed in the close vicinity of sample and connected with a sensitive digital micro voltmeter. The temperature of thermostat was increased in steps of 3°K for each measurement and kept constant for half-an-hour. A polaroid sheet is placed over the eyepiece to allow the distinct separation of dark and bright regions in the eyepiece corresponding to n_e and n_o [17].

The texture studies of E47 were also conducted using a polarizing microscope (OLYMPUS Model BX51) in conjunction with a hot stage (Linkam TP94 and THMS600) and high resolution CCD camera connect to computer. Heating and cooling were done at the rate of $\pm 1.0^\circ\text{C}/\text{min}$. The temperature of the sample was measured to an accuracy of $\pm 0.1^\circ\text{C}$ in a programmable temperature controller. Sample was first heated to temperatures well above the isotropic transition temperature and then allowed to cool. Texture photographs of the sample were taken in the nematic phase during cooling run.

4. Results and discussion

The clearing temperature of E47 as obtained by refractometer and polarizing microscope agree closely. The transition temperature is, however, not as sharp [24] as in the case of pure nematic liquid crystals which may be, due to different components in the mixture. Its seems that the different components in the mixtures undergo nematic isotropic transition through a sequence of co-existing nematic-isotropic phases. From a practical point of view, we therefore take the nematic-isotropic transition temperature, T_{Ni} , as when the nematic isotropic phases are present in equal amounts. The average value of the broad phase region is considered as $T_{MI} = 61 \pm 2^\circ\text{C}$.

To make a fair comparison of various properties of the sample all graphs have been plotted with reduced temperature (T/T_{Ni}). The constant A , B , Δn and β are calculated for the sample using eqs. (5) and (6) and their values are given in Table 1.

Table 1. Calculated values of constant A , B , Δn and β .

Sample	A	B	$(\Delta n)_o$	β
E47	1.7034	-0.0004326	0.2080	0.1253

In Figure 1, discrete points from observations and continuous curve from calculation as a function of reduced temperature for n_e and n_o and $(\langle n^2 \rangle)^{1/2}$ have been plotted. The closeness of the continuous curve with the experimental points validates the modified four parameter model. As temperature increases, behaviour of n_e is different from n_o ; n_e depends strongly on temperature. With the increase in temperature, n_e decreases throughout the entire nematic range while n_o increases initially slowly and

then increases rapidly. Near the isotropic temperature, there is a sudden decrease in rms refractive index because of first order in nature according to Landau rules. The rms refractive index decreases linearly as the temperature increases. Above the clearing point the optical anisotropy vanishes and the isotropic refractive index (n_i) decreases with temperature as in normal organic liquids [25–27].

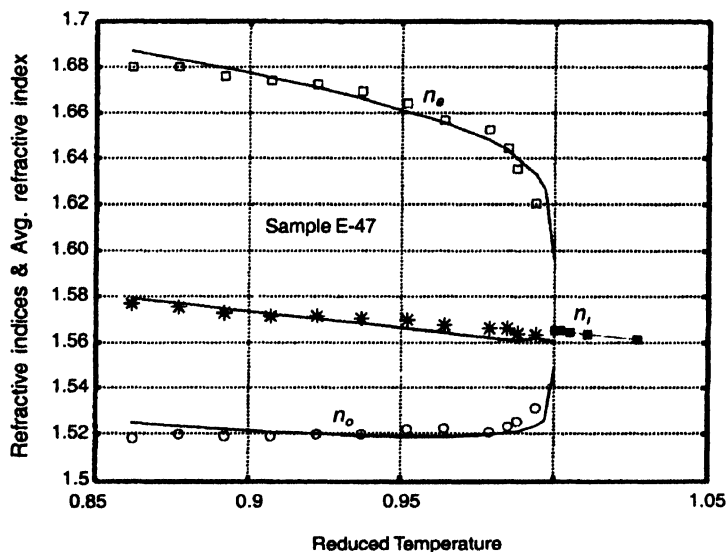


Figure 1. Temperature dependence of refractive indices n_e , n_o , n_i and n_{AVG} . Experimental data of n_e : (\square), n_o : (\circ), n_{AVG} : ($*$), n_i : (\blacksquare) and solid lines represent fitting curves of calculated data.

In Figure 2 is shown the temperature dependence of normalized polarizabilities for extraordinary (α_e/α_o) and ordinary (α_o/α_o) components. The normalized polarizabilities obtained are independent of density and reduce to unity in the isotropic phase. The actual mean polarizability and polarizability anisotropies of the mixtures may deviate from the additive rule of the components in the mixture.

In Figure 3, we have plotted the order parameter 'S' obtained experimentally, using modified four parameter model empirical equation correlate the refracting indices with the molecular polarizabilities and theoretical Maier-Saupe model for the singlet orientational distribution of the chain segments. The value of 'S' obtained using modified four parameter model agree more closely with the experimentally obtained 'S'. Moreover, the maximum percentage deviation of 'S' with the experimentally obtained values is just 7% in the case of modified four parameter values in contrast to 17% for modified theoretical Maier-Saupe model values. The 'S' value decreases with rise in temperature and reduce to zero as the temperature approaches at T_{NI} . This behaviour of 'S' is similar to that of birefringence and it is further verified by the linear relationship between these two factors (S and Δn), as shown in Figure 4.

The value of α_e/α_o as a function of temperature is shown in Figure 5. α_e/α_o decreases gradually with increase in temperature. This variation of α_e/α_o may be due

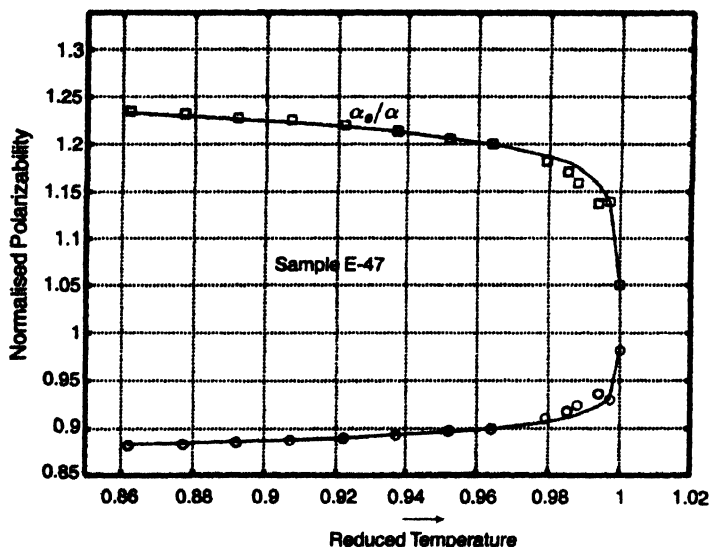


Figure 2. Temperature dependence of normalized polarizabilities, (□) and (○) are represent experimental data of α_e/α and α_o/α respectively and solid lines represent fitting curves of calculated data.

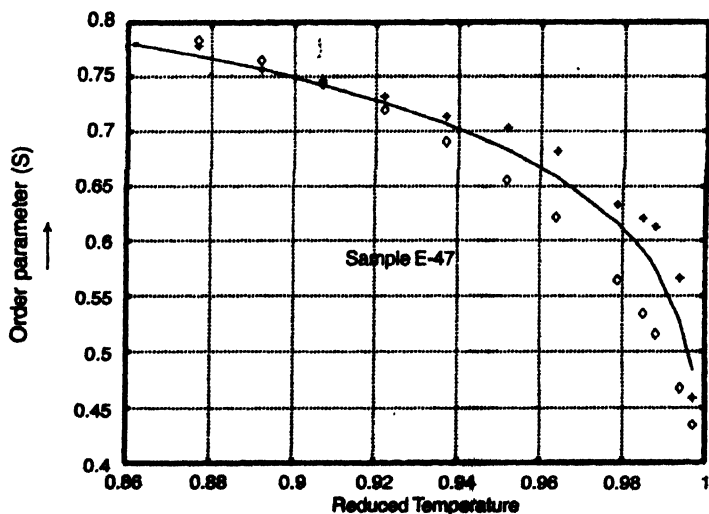


Figure 3. Temperature dependence of microscopic order parameter (S) : (*) represent experimental, (◊) represent modified Maier-Saupe approximation data and solid line represent fitting curves of calculated data using modified four parameter model.

to two factors, namely (a) the buckling of the end alkyl groups in the molecules and (b) the variation of the order parameter which is related to the orientation of the long molecular axis with respect to the director. Sama *et al* [26] and Krishnamurti [28] have shown that the buckling of the end alkyl groups increases with increase in temperature, thereby reducing α_e/α_o in the nematic phase of the mixture.

In Figure 6 are shown the optical micro-textures of the sample under crossed

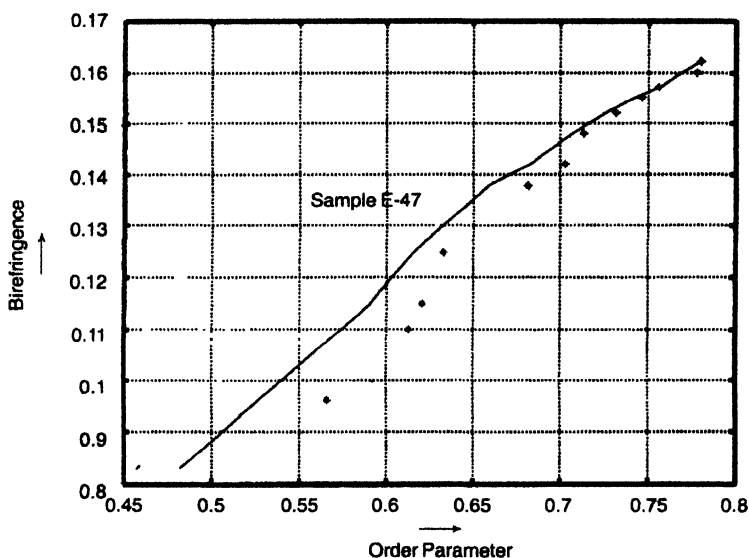


Figure 4. Order parameter versus birefringence (*) represent experimental data and solid line represent fitting curve of calculated data.

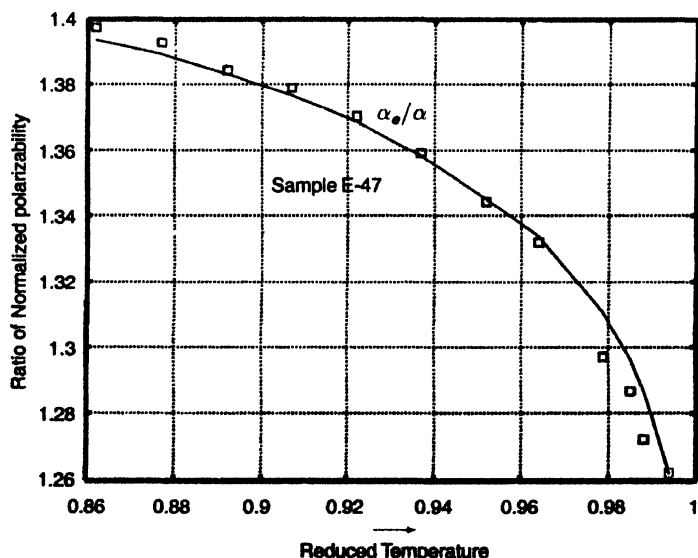


Figure 5. Temperature dependence α_o/α . Squares (□) represent experimental data points and solid line represent fitting curves of calculated data.

polarizer during cooling from its isotropic phase to nematic phase. The phase transition occurrence is exhibited by the change in optical texture and refractive index of the sample. The width of transition depends upon the purity of the substance and it increases with lower purity. Thus the composition of the mixture may be adjusted to give a narrow range of melting [28,29].



Figure 6. Textures of E47 at different temperatures (cell thickness 10 μm)

Acknowledgments

One of us, Jitendra Kumar Kushwaha is grateful to Mr. T N Soorya, Mr. Anant Kumar, and Mr. Sachin Jain, Department of Physics, Vardhman P G College, Bijnor, for the help in refractive index measurements and to Dr. Praveen Malik and Dr. Pankaj Kumar, School of Physics and Material Sciences, Thapar University, Patiala (Punjab) for the help with texture studies of the mesogen. We would like to thank Dr. B Bahadur, Display Center Design, Rockwell Collins, 400 Collins Road NE, Cedar Rapids, IA 52498-0001 (USA) for useful discussions.

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