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Ordering Behavior and Linear Dichroism of Pure and Doped Liquid Crystals

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In the present paper, C_7 liquid crystals' refractive indices have been measured throughout the nematic and isotropic phase, in order to determine the order parameter by using Vuks method and characterization of anisotropic behaviors. The temperature dependence of refractive indices, birefringence and order parameters in the anisotropic phase, has been investigated for this liquid crystal. Furthermore, the dichroic ratios of doped C_7 by linear azo dye, obtained on the basis of polarized absorption measurements. Then, the orientational ordering of the doped liquid crystal is analyzed by determining the order parameters, in different dye concentrations. The ordering behavior of a doped liquid crystal mixture is studied. It is found that even in very low compositional percentage of the dyes, the obtained order parameters are strongly affected by increasing the dye concentration.

Keywords Refractive indices; Vuks method; dichroism; doped liquid crystal; polarized spectroscopy

1. Introduction

Liquid crystals have many interesting and useful properties for particular application in many devices. The application of liquid crystals in different devises depends upon various properties such as the order parameter. It is well known that the characterization of liquid crystals' (LCs) properties is one of the most interesting research topics in the development and improvement of these materials for particular applications [1–6]. To enhance the physical and photo-physical properties of many electro-optical devices, various kinds of gust-host systems are used [7]. In these systems, the added material (guest) affects several parameters of the host which is due to the strong mutual interactions between the guest and the host molecules. The primary subject in doped liquid crystals is the qualitative determination of the order parameter [6, 7]. The polarized spectroscopy is one of the most informative tools in the study of conformation and orientaional order of the liquid crystal materials. Furthermore, spectroscopic method provides further information about the intermolecular interactions in the doped anisotropic matrixes [8].

In this work, we have studied C_7 mixture nematic liquid crystal with high chemical and thermal stability. This study comprises the determination of the birefringence, ordinary

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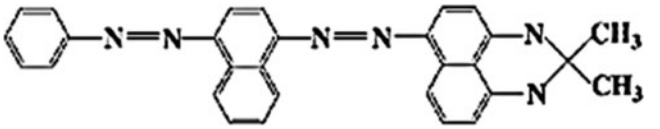
and extraordinary refractive index, macroscopic and microscopic order parameters and also temperature dependence of these parameters. Furthermore, the linear dichroism and order parameter of doped C_7, with different compositional percentage of azo dye molecules was obtained on the basis of polarized absorption measurements. The polarized spectroscopy was used to analyze the orientational ordering of the liquid crystal-dye mixtures. The different compositional percentage of dye molecules were used to obtain information about the effect of dopants' compositional percentage on the orientational ordering of the dye-doped liquid crystals. Finally, the order parameters of the doped liquid crystal were determined by using Vuks and linear dichroism method and compared to the order parameter of pure C_7.

2. Experimental Method

2.1. Materials

The eutectic nematic mixtures of C_7 with positive birefringence were used as anisotropic hosts in our experiments. The nematic to isotropic transition temperature (clearing temperature) for this sample is 60°C. Sudan black B (Fig. 1) were obtained from BDH (pro-analysis) and used without further purification as solutes (guests). Dye-doped liquid crystal solutions were prepared by dissolving the dyes with different compositional percentage, about 0.5%, 1%, 3% W/W, in liquid crystal solvent.



Sudan black B

Figure 1. Molecular structure of Sudan black B dye.

2.2. Refractive Index Measurements

Refractive index has been measured using Abbe's refractometer having an accuracy of 0.00001 in the range of 1.2 to 1.74 (Bellingham Stanley Abbe 60 ED). A polarizer sheet has been introduced clears contrast of the boundary line for ordinary and extraordinary ray in Abbe's refractometer. The temperature of Abbe's refractometer was controlled by circulating silicone oil in the oil bath temperature controller. The temperature was measured by placing a thermometer in close vicinity of the sample with an accuracy of ± 0.1°C. While the ordinary and extraordinary refractive index, n_o and n_e, in the nematic phase has been directly measured.

2.3. The Liquid Crystal Cell Preparation for Polarized Spectroscopy

The guest- host cells were made by sandwiching the solutions between two glass plates (1.2×4.5 cm^2). The planar orientation of the cell with the homogeneous alignment of the host and guest molecules was achieved by the surface treatment of the glass plates with poly vinyl alcohol (PVA) and additional robbing process [9]. The liquid crystal cells were designed to have thickness of 20 μm, using Mylar spacers. The cells were filled with the chosen samples by capillary action.

2.4. Determination of Order Parameter by Using Vuks Method

The orientational order parameter was calculated by means of the Vuks assumption [10]:

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

where $\Delta\alpha$ $(= \alpha_{II} - \alpha_{\perp})$ is the anisotropy of polarizability and α is the mean molecular polarizability. To determine$\left(\frac{\Delta\alpha}{\alpha}\right)$, plot of linear part of ln $\left[\frac{3(n_e^2-n_o^2)}{n_e^2+2n_o^2-3}\right]$against ln $\left(1 - {}^{T}/_{T_c}\right)$can be extrapolated to T = 0 K. The intercept at T = 0 K, where completely ordered structure exist i.e. S = 1, gives the value of scaling factor$\left(\frac{\Delta\alpha}{\alpha}\right)$. Assuming that$\left(\frac{\Delta\alpha}{\alpha}\right)$remains fixed for all the temperatures and substituting this value into Eq. 1, one can obtain values of order parameter at different temperatures. Thus, the smaller scaling factors and the larger values of $\left(\frac{n_e^2-n_o^2}{\langle n^2\rangle-1}\right)$ render higher values for microscopic order parameter.

2.5. Determination of Dichroic Ratio and Order Parameter by Using Linear Dichroism

The experimentally dichroic ratio (R) is defined as $R = A_{\parallel}/A_{\perp}$ [11, 12], where $A_{\parallel}$ and $A_{\perp}$ are the absorbances for light polarized parallel and perpendicular to the director, respectively. The dichroic ratio of a uniaxial nematic liquid crystal can be related to the order parameter by the following equation [13–15]:

$$S = \frac{(R-1)}{(R+2)}\frac{2}{3\cos^2\alpha - 1}, \tag{2}$$

in which α is an angle between the long molecular axis and the transition dipole moment of the liquid crystal. If the transition moment is directed along the long axis of the molecule (), Eq. (3) reduces to

$$S = (R-1)\big/\,(R+2). \tag{3}$$

The polarized absorption spectra of the guest-host mixtures in the Vis spectral region were measured using a spectrometer (Model HR 4000 CG, UV-NIR), equipped with sheet polarizers. The measurements were performed at room temperature and the dichroic ratio was calculated using $R = A_{\parallel}/A_{\perp}$. The direction of the polarization of the light to determine $A_{\parallel}$ and $A_{\perp}$ is shown in Fig. 2.

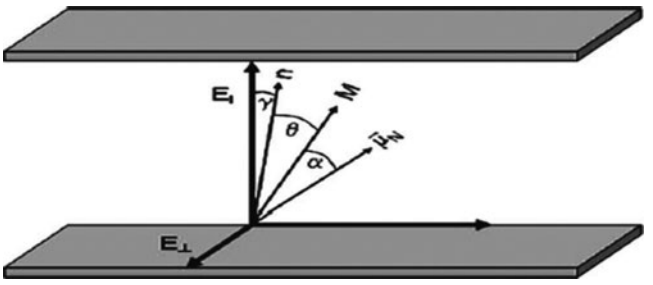


Figure 2. Scheme of vectors of polarized light electric fields, the director, molecular long axis for individual molecule (M) and the transition dipole moment of a dye molecule, with respect to the cell plates.

3. Results and Discussion

3.1. Refractive Indices and Order Parameter of the C_7 LC

The temperature variations of the experimental data for ordinary and extraordinary refractive indices (n_e, n_o) are shown in Fig. 3, for C_7 liquid crystal. Large polarizability of the LC in the direction of the long molecular axis leads to a positive optical anisotropy (i.e. $n_e > n_o$) over the entire nematic phase. The refractive index values change rapidly for nematic–isotropic phase transition in the investigated LC. As the temperature increases, the ordinary refractive index increases slightly, while the extraordinary refractive index decreases sharply.

The order parameter (S) of investigated LC was calculated from refractive indices data and the Vuks approach, Eq. (1), scaling factors for this LC is 0.66. This scaling factor amount is higher than some investigated LCs such as cyano-benzoate [6] and carboxylate [16] nematic liquid crystals. Therefore, despite the fact that refractive indices and $\left(\frac{n_e^2-n_o^2}{\langle n^2\rangle-1}\right)$ have large amounts, the order parameter values of C_7 show average amounts. The obtained result is represented in Fig. 4.

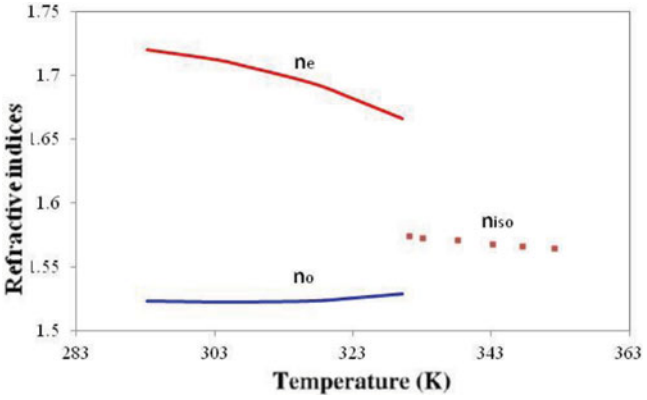


Figure 3. The temperature variations of the experimental data for ordinary and extraordinary refractive indices (n_e, n_o).

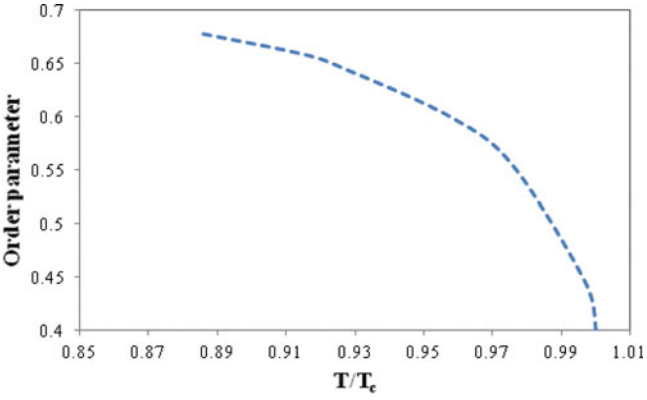


Figure 4. The temperature variations of the obtained order parameter in Vuks method.

Table 1. Dichroic ratios R and order parameters S measured for the Sudan black B dye in C_7LC media

Compound	Compositional percentage W/W(%)	$\lambda_{max}(nm)$	R	S
Sudan black B	0.5	604.95	6.1	0.63
	1	606.24	6.0	0.62
	3	614.75	5.2	0.59

3.2. Dichroic Ratio and Order Parameter of the Dye Doped C_7 LC

The analysis of the influence of the solvent properties on the absorption spectra of the dye was performed on the basis of the polarized absorption measurements. The main absorption band of the Sudan black B in visible region corresponds to a transition moment largely parallel to the long axis of the molecules due to π–π^* transition (localized in the azo group). The solvation of Sudan black B dye molecules in the liquid crystalline host can be affected by additional anisotropic interactions between the dye and anisotropic host environment and strong solvent–solvent interaction [9].

The polarized absorptions of Sudan black B was measured in parallel-aligned liquid crystal cells and their dichroic ratios were obtained. Also, the maximum absorption wavelengths of the Sudan black B dye, in liquid crystal solvent (0.5%, 1%, 3% W/W) and the obtained order parameters are reported in Table 1.

The experimental results for different compositional percentages of the Sudan black B, given in the Table 1, show that in high compositional percentage of the dye, the obtained order parameters decrease by increasing the dye concentration. In addition, the spectra of the Sudan black B dye in liquid crystalline host exhibit a band broadening by increasing the dye concentration (Fig. 5). It should be noted that the value of S might differ from the order parameter for the molecular axis S_M. This is the case when there is an angle between the transition moment and the long molecular axis [8]. The dichroic ratio is directly related to the order parameter for the transition moment and therefore, the molecular structure of dopants has high effect in order parameter for doped LC. In other words, the orientation of

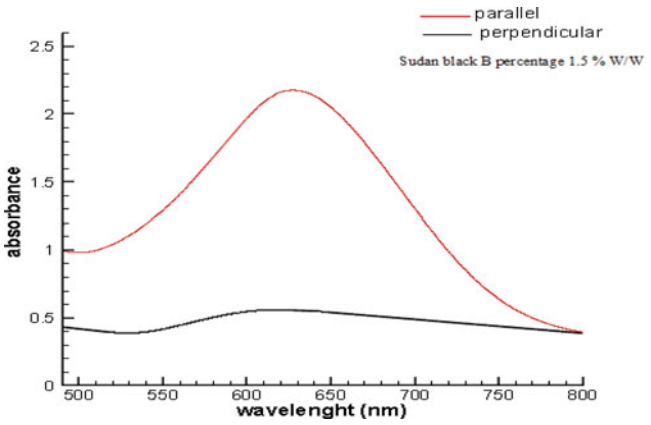


Figure 5. Polarized absorption spectra of the Sudan black B dye in the oriented C7 mixture (∼1.5%,).

LC molecules causes the dye molecules ordering and, hence, the obtained dichroic ratio is related to transition moment of Sudan black B.

These results confirm that, as the structure and shape of the dye and C_7 liquid crystalline solvent molecules are compatible, as in low concentration of Sudan black B with high polarity [17] and rod-like molecular shape, the dye molecules can be incorporated into the liquid crystalline matrix without disrupting its order which is in agreement with our previously reported results [9]. By increasing the concentration of Sudan black B in C_7 LC media, the guest-guest (dye-dye) interaction decreases the initial ordering applied by LC molecules and then it leads decreasing of the order parameter of the doped C_7 LC system.

4. Conclusion

The order parameter (S) of C_7 LC was calculated by using two methods. The obtained values for order parameter by using two different methods show dissimilar amounts. In Vuks approach, the LC show order parameter amount of 0.66 in 22°C due to the large amounts of the refractive indices of C_7. On the other hand, by using the other method, the liquid crystal doped by low amount of a linear dye (Sudan black B) demonstrate the order parameter value of 0.61 in 22°C. It should be noted that the two used methods are completely different in nature. In other words, in Vuks method, structural parameters of LC are used for calculation of the order parameter, but in the other method, in addition to liquid crystal structural parameters, environmental factors, such as dye concentration and LC cell preparation robbing process, play significant roles. This method can be applicable in really commercial system such as guest–host LCDs.

The order parameter (S) of investigated C_7 was calculated from refractive indices data and the Vuks approach. The scaling factor for this LC is 0.66. This scaling factor amount is higher than some investigated LCs. It was found that the alignment properties of the guest–host system can be critically affected by concentration of the dye. In other words, the director orientation can be altered by amount of the dye. In fact, the dye molecules can be incorporated into the liquid crystalline matrix without disrupting its order in low concentration. By increasing the concentration of Sudan black B in C_7LC media, the guest-guest (dye-dye) interaction decreases the initial ordering applied by LC molecules and therefore, leads decreasing the order parameter of doped C_7LC system.

References

[1] Muenster, R., Jarasch, M., Zhuang, X., Shen, Y. R. (1997). *Phys. Rev. Lett.*, *78*, 42.
[2] Philip, J., Prasada Rao, T. A. (1992). *Phys. Rev. A*, *46*, 2163.
[3] Pouligny, B., Marcerou, J. P., Lalanne, J. R., Coles, H. J. (1983). *Mol. Phys.*, *49*, 583.
[4] Khoo, C. (2009). *Physics Reports*, *471*, 221–267.
[5] Zakerhamidi, M. S., Ebrahimi, Z., Tajalli, H., Ghanadzadeh, A., Moghadam, M., Ranjkesh, A. (2010). *J. Mol. Liq.*, *157*, 119.
[6] Zakerhamidi, M.S., Rahimzadeh, H. (2012). *J. Mol. Liq.*, *172*, 41.
[7] Khoo, I. C. (2007) *Liquid Crystals, 2nd* ed., Wiley, New York.
[8] Ghanadzadeh, A., Zakerhamidi, M. S. (2004). *J. Mol. Liq.*, *109*, 149.
[9] Ghanadzadeh, A., Shahzamanian, M. A., Shoarinejad, S., Zakerhamidi, M. S., Moghadam, M. (2007). *J. Mol. Liq.*, *136*, 22.
[10] Vuks, M. F. (1996). *Optika i Spektroskopiya*, *20*, 644.
[11] Meier, G., Sackmann, E., Grabmaier, J.G. (1975) *Application of Liquid Crystals*, Springer Verlag, Berliny Heidlberg.
[12] Michl, J., Thulstrup, E. W. (1995) *Spectroscopy of Polarized Spectroscopy*, VCH Book.

[13] Park, Woo-Sang (2000). *J. Korean Phys. Soc.*, *37*, 331.
[14] Korte, E. H. (1983). *Mol. Cryst. Liq. Cryst.*, *100*, 127.
[15] Shoarinejad, S., Zakerhamidi, M. S. (2011). *Mol. Cryst. Liq. Cryst.*, *547*, 135.
[16] Zakerhamidi, M. S., Rahimzadeh, H. (2012). *Mol. Cryst. Liq. Cryst.*, *569*, 92.
[17] Zakerhamidi, M. S., Golghasemi Sorkhabi, Sh., Shamkhali, A. N. (2014). *Spectrochimica Acta Part A: Mol. Bio mol. Spect.*, *127*, 340.