Molecular dynamics in weakly polar nematic liquid crystal doped with dye

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Abstract: Our intention in the present work is to find out the role of dye in the molecular orientation of the weakly polar nematic liquid crystal D6AOB. The doping of a dye introduces a disturbance in the molecular arrangement of the nematic liquid crystal molecules. However, this disturbance is found to be sensitive to the concentration of the dye dispersed in the nematic liquid crystal. It is found that orientation in the dyed nematic liquid crystal is less ordered than the orientation in the pure nematic liquid crystals. This behavior has been explained on the basis of intermolecular interaction, i.e., dipole–dipole interaction.

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Résumé : Notre but ici est de déterminer le rôle du colorant dans l’orientation moléculaire du cristal liquide nématique faiblement polaire D6AOB. Le dopage par un colorant introduit une perturbation dans l’arrangement moléculaire des molécules du cristal liquide némagique Cependant, nous observons que cette perturbation dépend de la concentration du colorant dispersé dans le cristal liquide némagique. Nous trouvons que l’orientation dans le cristal liquide némagique coloré est plus faible que dans le cristal liquide némagique sans colorant. Ce comportement s’explique sur la base de l’interaction intermoléculaire i.e., l’interaction dipôle–dipôle.

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1. Introduction

Composite liquid crystal (LC) systems, such as liquid crystal mixtures with organic and inorganic nanoparticles [1, 2], polymer dispersed liquid crystals [3], dye-doped liquid crystals [4, 5], etc., have been studied a great deal in recent years. These guest-host liquid crystals (GHLCs) are now used to produce optical contrast in display devices. These GHLCs have other advantageous features over conventional displays, such as vivid color, high brightness, and large viewing angle. The research community has now focused their attention on the application of these GHLCs in light valve arrays, recording media, dye-doped solar cells, etc. [6].

Most investigations on dye-doped liquid crystals are concentrated around their electro-optical properties and also on those properties that affect the performance of the practical devices directly [7, 8]. Dye-doping changes the intermolecular interaction of pure LC molecules considerably and results in changes in the molecular dynamics of pure liquid crystals. The orientation ordering in dye-doped liquid crystalline systems depends on the shapes of both the liquid crystal molecule and the dye molecule, and the intermolecular attraction that mainly arises from anisotropic short-range and long-range forces [9]. The key role is played by the dipole–dipole interaction of molecules, either from a permanent or induced dipole moment. As such, a detailed knowledge of long-range interactions is needed, as these have not yet been completely understood. Therefore, it is important to understand the role of long-range interactions on the molecular dynamics of the system. To understand the relationship between dielectric permittivity and molecular properties has long been an objective of many dielectric studies [10–12].

Dielectric relaxation spectroscopy and electro-optical studies are important tools in understanding the molecular dynamics of liquid crystal systems. The large frequency range offered by the dielectric spectroscopic method makes it ideal for studying the dynamics of dipolar motions that could exist in a wide range of frequencies. Various dielectric investigations on liquid crystals have already been reported, but most of the studies have involved molecules having a strong dipole moment [13, 14]. Our group has also reported experimental results on dielectric and electro-optical properties of pure and doped liquid crystals [15, 16]. The present paper is an attempt to develop a clear picture for molecular ordering in dyed nematic liquid crystals.

2. Experimental details

2.1. Material

The investigated system consists of weakly polar nematic liquid crystal material D6AOB (4-4′-Dihexyloxazobenzene). The anthraquinone dyes used in our investigation are Solvent green 3 (SG3) and D37. For the study of a guest-host system,
we have used D6AOB doped at a dye concentration of about 0.5%, 1%, and 2% w/w ratio. The doped mixtures were prepared by the dispersion of dye in the nematic liquid crystal. The transition temperatures of the pure compound, their structural formula, and the chemical names are shown in Fig. 1.

2.2. Preparation of sample cell

Sandwiched-type cells were prepared for the measurement of dielectric permittivity using transparent and a highly conducting ITO coated glass substrate. The liquid crystal alignment, parallel or perpendicular to the electrode surfaces, was achieved by applying different surface treatments to the cells for parallel (rubbed Nylon6/6) or perpendicular (Cetyl trimethylammonium bromide in ethyl alcohol). The alignment of the liquid crystal director perpendicular to the electrode surface enables $\varepsilon_{\parallel}$ (field parallel to the long molecular axis) to be measured, while if the director is aligned parallel to the electrode surface, then the permittivity component measured is $\varepsilon_{\perp}$ (field perpendicular to the long molecular axis). The thickness of the cell was maintained at 10 $\mu$m with the help of a Mylar spacer. The cell was calibrated using AR grade carbon tetrachloride (CCl4) and benzene. The material was introduced into the cell by capillary action at a temperature above the isotropic temperature of the sample.

2.3. Dielectric measurement

The dielectric response of the sample was studied in the frequency range of 100 Hz to 40 MHz, using a computer-controlled impedance–gain phase analyzer (HP-4194A). The temperature of the sample cell was achieved by using Instec hot plate (HCS-302), with an accuracy of ±0.1 °C. The sample was left for 10 min before starting the measurement at a particular temperature. All the data reported here concentrates on the dielectric properties in the nematic phase of the mixture.
3. Results

The dielectric response of liquid crystals shows complex behavior as a function of both frequency and temperature. The dielectric data has been analyzed using the Cole-Cole equation, given as,

\[ \varepsilon^\prime = \varepsilon^\prime(\infty) + \frac{\delta \varepsilon}{1 + (i \omega \tau)^{1 - \alpha}} \]  

(1)

where \( \delta \varepsilon \) is the dielectric strength, \( \varepsilon^\prime(\infty) \) is the high-frequency limit of dielectric permittivity, \( \omega \) \( (2\pi f) \) is the angular frequency, \( \tau \) is the relaxation time, and \( \alpha \) is the distribution parameter for the relaxation time. On separating the real and imaginary parts of (1), one may obtain, after adding high- and low-frequency correction, the fitting parameters. The terms \( \frac{\delta \varepsilon}{1 + (2\pi f \tau)^{1-\alpha}} \) and \( \frac{\delta \varepsilon}{1 + (2\pi f \tau)^{2(1-\alpha)}} \) are included in the above equation for the low-frequency effect due to the electrode polarization, capacitance, and ionic conductance. The term \( \frac{\delta \varepsilon}{1 + (2\pi f \tau)^{1-\alpha}} \) is added in the equation for the high-frequency effect due to the ITO sheet resistance and lead inductance of the cell. By least-squares fitting of experimental data to the above equation, the low- and high-frequency data have been corrected.

To see the effect of the dye on the dielectric properties of the liquid crystal, \( \varepsilon_0 \), \( \varepsilon_\perp \), and \( \Delta \varepsilon \) have been measured for pure and dye-doped samples at different concentrations of the dye.

Figure 2 shows the variation of \( \varepsilon_\parallel \) with frequency for both pure and the dye-doped samples at a constant temperature, 40 °C. Figure 3 shows the variation of \( \varepsilon_\perp \) with frequency for both pure and dye-doped samples at 40 °C. The dielectric permittivity behavior of the guest-host system is almost the same as that of the pure nematic liquid crystal; however, the values observed for GHLCs is found to be lower, compared with the pure system.

The dielectric anisotropic behavior of both dye-doped systems is shown in Fig. 4 as a function of temperature, at 10 kHz.

4. Discussion

The above results can be explained on the basis of the dipole moment orientation of the nematic molecules. The earlier results suggest that dipole moment of the D6AOB molecule lies at an angle of around 64° to its long molecular axis [18, 19], which according to the Maier-Maier theory [20] leads to negative dielectric anisotropy. However, the contribution of electronic polarizability to \( \varepsilon \) is greater in the direction along the long molecular axis than perpendicular to it. This makes the dielectric anisotropy positive. The value of dipole moment in the literature is given as 1.70 D [18] (1 D = 10⁻¹⁸ statcoulomb-centimeter). The structure of the dye also suggests that its dipole moment should be small.

In an homeotropically aligned cell, the contribution to the dielectric permittivity of the dipole moment of the D6AOB molecule in the direction parallel to the electric field, i.e., \( \varepsilon_\parallel \), is small, and is large in the perpendicular direction. When a dye is introduced into the liquid crystal matrix, the dye molecules try to fit into the geometry of the nematic system. However, if the structure of the dye molecule is not exactly rod-like (similar to LC molecules), it will introduce some disorder in the nematic system, at least in the area around dye molecules. This is the case in our system. This disorder will
surely decrease the value of $\varepsilon_\|^{}$, as found in our experiment. At low concentration, the disorder caused by the dye molecules is low, but as the concentration is increased the disorder will also increase.

In the case of a planar aligned cell, the nematic molecules are oriented parallel to the rubbed glass surface and perpendicular to the applied electric field. Since the dipole moment is oriented at an angle of almost 64° to the direction of the long molecular axis, therefore the value of $\varepsilon_\|^{}$ is higher compared with $\varepsilon_\perp$. The dye-induced disorder in the system causes variation in the value of $\varepsilon_\perp$ as observed for 0.5% dye-doped system for both dyes. The large change in $\varepsilon_\perp$ for 0.5% D37 doped nematic system might be due to the injected impurities during the experimental procedure. One change that is noticed here is the variation of dielectric permittivity $\varepsilon_\perp$ for 1% and 2% dye-doped system of D37 dye. The dipole-induced disorder in the system causes variation in the value of $\varepsilon_\perp$ as observed for 0.5% dye-doped system for both dyes. The large change in $\varepsilon_\perp$ for 0.5% D37 doped nematic system might be due to the injected impurities during the experimental procedure. One change that is noticed here is the variation of dielectric permittivity $\varepsilon_\perp$ for 1% and 2% dye-doped system of D37 dye. It appears that the molecule in this system, i.e., for 1% and 2% D37-doped D6AOB, is more ordered than the other systems. The dipole moment of the dye will also contribute to the dielectric permittivity $\varepsilon_\perp$. In the SG3 dye-doped system, the dielectric permittivity $\varepsilon_\perp$ shows a regular decreasing trend with increasing concentration of dye in the nematic system. This behavior of dielectric permittivity for an SG3-doped system shows the increasing disorder in the system with increasing concentration.

When a dye is introduced into the LC matrix, the disturbances caused around dye molecules form domains. These domains are randomly oriented within the LC matrix, which results in a decrease in the value of the dielectric permittivity. At lower concentrations of the dye, the distance between these domains are large, which means that there is almost no interaction between the domains, but when we increase the concentration of dye in the LC matrix, the number of domains within the system increases. Therefore, the distance between the domains decreases, and they start interacting

**Fig. 3.** Dielectric permittivity $\varepsilon_\perp$ versus applied frequency at 40 °C for (a) dye D37 and (b) dye SG3.

**Fig. 4.** Dielectric anisotropy $\Delta\varepsilon$ versus temperature (at 10 kHz) for (a) dye D37 and (b) dye SG3.
with each other. The major role played here is by the dipole–dipole interaction of the dye molecule. This interaction will cause the domains to follow the nematic orientation, therefore an increase in the value of the dielectric permittivity is observed. However this effect will not be visible in all dyes. Such behavior will depend upon the molecular parameters of dye, i.e., molecular structure, length, and orientation and value of the dipole moment of dye. Also, there must be some saturation concentration up to which there will be an increase in the value of dielectric permittivity. We have not observed any saturation concentration in any system. For SG3-doped systems, all the concentrations of dye in the nematic system show a decreasing trend in dielectric permittivity, in both planar and homeotropically aligned cells. But for D37-doped systems, 1% and 2% concentration of dye shows the presence of these interactions in the case of planar aligned cells ($\varepsilon_{\perp}$).

The dielectric anisotropic behavior of dye-doped system is shown in Fig. 4. According to the Maier-Maier theory,

$$\Delta \varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp} = \frac{N_0 \mu b}{\varepsilon_0} \left[ \Delta \alpha - \frac{F \mu^2}{2KT} \left( 1 - 3 \cos^2 \beta \right) \right] S$$

(4)

The value of $\Delta \varepsilon$ is proportional to $S$, molecular polarizability, and the orientation of dipole moment. The orientation of the dipole moment is governed by the angle $\beta$, which is the angle between the direction of the dipole moment with the long molecular axis. However, there will be small changes in $S$ when the concentration of dye is too small. Therefore, $\Delta \varepsilon$ is totally governed by the orientation of the nematic molecule, which depends upon the concentration of dye introduced into the nematic matrix.

5. Conclusion

In this work, the experimental data points out the role of concentration of a dye in the molecular ordering of a weakly polar nematic liquid crystal in a dye-doped system. The order in the dye-doped system is found to be sensitive to the presence of the dye concentration in the LC matrix. Hence in the dye-doped system of nematic liquid crystal, the order of the system is not only governed by the confining walls but also by the dye molecules. The concentration of the dye plays an important role in the determination of molecular ordering. Below a certain concentration of the dye (known as critical concentration), where the interaction between the dye molecules can be neglected, it introduces a disorder in the system. Above the critical concentration, this disorder is less. Dipole–dipole interaction between the dye molecules causes the refinement of interaction energies of the rod-like nematic liquid crystal molecule and anthraquinone dye.

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