

Effect of nano particles on the dielectric anisotropy of liquid crystal

Kamal Kumar Pandey¹, Amit Kumar Bawaria², Poonam Priyadarshi³

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To study the effect of nanoparticles on the anisotropy of weakly polarized nematic liquid crystal (D6AOB), dielectric measurements were carried out in the frequency range 100 Hz to 40 MHz at bias voltage of 0.5V and in the voltage range from 0V to 40V at 100 Hz. The dielectric data were measured for two principal alignments; one is homeotropic and other is planar. The dielectric anisotropy ($\Delta\epsilon$) were studied with variation of frequency, temperature and voltage. The angle β between the long molecular axis and dipole moment of the molecules are calculated from Cole-Cole plot by using Onsager theory, both for pure and doped liquid crystal. It is found to decrease for the doped sample. The $\Delta\epsilon$ is explained by Maier and Meier theory. Here is also an attempt to discuss the $\Delta\epsilon$ versus voltage on the basis of piezoelectric strain and which has found in good agreement with experimental results.

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15 Introduction

In recent years, full colour and flat screen liquid crystal displays (LCDs), which are almost indispensable in many fields, have aroused much interest in the study of LCs. These LC devices are known to operate in the frequency region of few hertz (Hz) to several mega hertz (MHz) that involves different modes of their molecular motions. Since these molecular motions involve both collective and noncollective type's dipolar studies, hence it evolves as a powerful tool to study the LCs molecular properties [1, 2]

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Recently the modifications of the physical properties of LCs by doping nano particles have received much attention from the view point of the enhancement of the performance of electro-optical LC devices. Reflecting these trends several groups reported all heterogeneous LC suspensions using ferromagnetic particles, ferroelectric nano particles, fullerene, the nano particles of metals such as Pd, Ag, Ag/Pd; inorganic nano particles of MgO; Carbon nano tubes and polymeric nanostructures [3, 4]. Such doping structure motivates to find the effect of zinc oxide nano particles (ZONPs) on the dipole dynamics and the molecular properties of LCs in the view of excellent atomic and electrical properties of ZONPs [5]. The dispersion and alignment of ZONPs in LCs may find to improve the mechanical, electrical, thermal and optical properties of bulk LC materials [6].

Dielectric anisotropy of LCs cause director reorientation in the applied electric field leads to the phenomenon of director reorientation in the electric field. This Fredericks effect is a well known phenomenon that has numerous applications, most notably in LC displays [7-9]. Hence the deep insights towards the dipole dynamics and dielectric anisotropy is required to understand the mechanism behind the variation of these properties with various parameters such as temperature, frequency, voltage etc [10, 11]. The study of nematic LCs having the weak dipole moment when doped with ZONPs may provide some additional information about the molecular properties [12,13]. In this investigation the inorganic ZONPs has been dissolved into a weakly polar nematic LC at a low weight concentration to form a nano nematic

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suspension. Our aim is to study the influence of ZONPs on the anisotropy of the system.

55 Experimental details

Materials

ZONPs doped LC suspension of a nematic LC host, 4, 4'-Di Hexyl Azoxy Benzene (D6AOB) have been used for the present investigations.

The host sample has been purchased from Flintron Laboratories U.S.A. The nanoparticles (Provided by the Nano Phosphor Centre, Physics Department, University of Allahabad, Allahabad 211002, India) were synthesized by a chemical technique based on hydrothermal method. The crystallite sizes, estimated by XRD were found to be nearly 14 nm, whereas TEM/SEM (Tunnelling Electron Microscopy / Scanning Electron Microscopy) studies showed formation of uniform nanorods [14]. At room temperature, Nanoparticles of ZnO are wide band gap (3.38 eV) semiconductor and also have the piezoelectricity [5].

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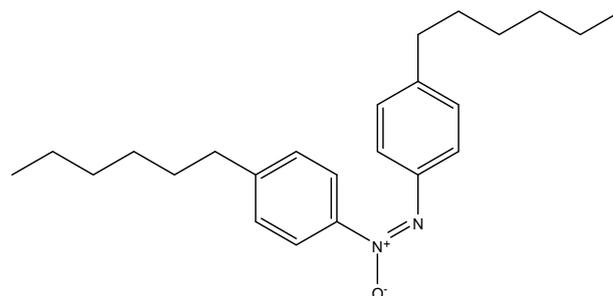


Fig. 1 Chemical structure of D6AOB (4, 4'-Di Hexyl Azoxy Benzene) molecule

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Dielectric measurement

Dielectric measurements were carried out using a computer controlled Gain/Phase analyzer (HP 4194A) attached with a temperature controller in the frequency range 100 Hz to 10MHz.

The dielectric measurements have been carried out as a function of temperature by placing the sample on a computer controlled hot plate (HCS-302, INSTEC Co. USA). The temperature stability was better than $\pm 0.1^{\circ}\text{C}$ within the measurement. The data obtained at higher frequencies were strongly affected by the ITO relaxation [15, 16], therefore data at $f > 10\text{MHz}$ are omitted.

The dielectric relaxation phenomena for both the samples in nematic phase have been examined using Cole-Cole relation. The Cole-Cole [17], equation is given by

$$\epsilon^* = \epsilon'(\infty) + \frac{\delta\epsilon'}{1 + (j\omega\tau)^{1-\alpha}} \quad (1)$$

Where $\delta\epsilon'$ is the dielectric strength of the relaxation and $\epsilon'(\infty)$ is high frequency limit of the relative dielectric permittivity, $\omega (= 2\pi f)$ is the angular frequency and τ is the relaxation time.

The low and high frequency deviations in dielectric data require correction for low and high frequency values. On separating the real and imaginary part of the equation (1) one may get

$$\epsilon' = \epsilon'(\text{dc})f^{-n} + \epsilon'(\infty) + \frac{\delta\epsilon'[1 + (2\pi f\tau)^{(1-\alpha)} \sin(\alpha\pi/2)]}{1 + (2\pi f\tau)^{2(1-\alpha)} + 2(2\pi f\tau)^{(1-\alpha)} \sin(\alpha\pi/2)}$$

And

$$\epsilon'' = \frac{\sigma(\text{dc})}{\epsilon_0 2\pi f^k} + \frac{\delta\epsilon'(2\pi f\tau)^{(1-\alpha)} \cos(\alpha\pi/2)}{1 + (2\pi f\tau)^{2(1-\alpha)} + 2(2\pi f\tau)^{(1-\alpha)} \sin(\alpha\pi/2)} + Af^m$$

Here $\sigma(\text{dc})$ is the ionic conductance and ϵ_0 is the free space permittivity; k, A and m are the fitting parameters; α is the distribution parameter and ω is the angular frequency. The term $\epsilon'(\text{dc})/f^n$ and $\sigma(\text{dc})/\epsilon_0 2\pi f^k$ are added in the above equation for the low frequency effect due to the electrode polarization, capacitance and ionic conductance. The term Af^m is added in equation 1b for the high frequency effect due to the ITO resistance and lead inductance [16, 17]. By the least square fitting of above equation into the experimental data we have removed the low and high frequency errors.

Results and discussion

The anisotropy and its dependence on frequency [$\epsilon_{\parallel} - \epsilon_{\perp}$] is usually explained within the framework of orientation of dipoles. In our case ϵ_{\parallel} and ϵ_{\perp} corresponds to the mechanism of nematic LC dipole polarization connected with rotations of rigid bar shaped molecules around the long and short axis respectively [18].

In the nematic phase the substances exhibit a positive dielectric anisotropy, $\epsilon_{\parallel} - \epsilon_{\perp} > 0$ at low frequencies as shown in figure 2.

However at MHz frequencies $\epsilon_{\parallel} - \epsilon_{\perp}$ decreases significantly and ultimately changes its sign for both pure D6AOB and ZONPs doped suspension. But the dielectric anisotropy of doped sample changes its sign from positive to negative just before the

megahertz region and variation is from the value of +0.2 to -0.2 around 1 MHz. This is due to the dispersion of the parallel dielectric permittivity component and a flat behaviour of the perpendicular component over broad range of the frequency. Such behaviour of the dielectric anisotropy has been also earlier reported for other LCs compounds having different chemical structures. This effect enables a dual addressing of the displays based on these substances [19, 20].

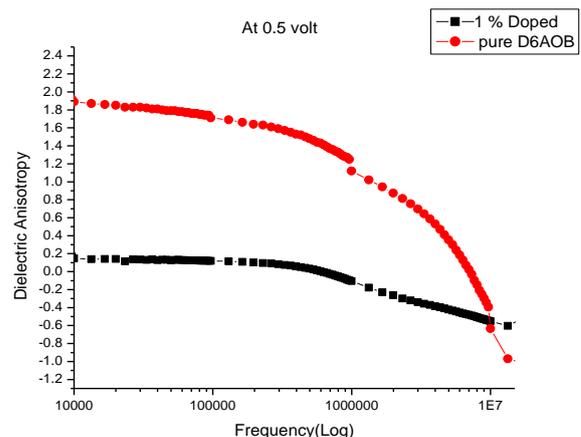


Fig. 2 Frequency dependence of the dielectric anisotropy for pure and doped samples

According to Maier and Meier [26], the dielectric anisotropy is given by

$$\Delta\epsilon = \epsilon_{\parallel} - \epsilon_{\perp} = \frac{N_0 h F}{\epsilon_0} \left\{ \Delta\alpha S - \frac{F\mu^2}{2KT} (1 - 3\text{Cos}^2\beta) S \right\} \quad (2)$$

Where ϵ_0 is the permittivity of free space, N_0 is the number density ($= N_A \rho / M$; $M = \text{Molar Mass}$, $\rho = \text{Density}$, $N_A = \text{Avogadro number}$) and S is the order parameter. The local field factor h and F are dependent upon the mean dielectric permittivity $\langle\epsilon\rangle$, $\langle\epsilon\rangle = (\epsilon_{\parallel} + 2\epsilon_{\perp})/3$.

The estimation of angle β (between the long molecular axes and the dipole moment of the molecules for the pure and the doped sample) have been done by following approach.

By applying the Onsager equation [9, 20]

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$$\frac{(\epsilon_s - \epsilon_{\infty})(2\epsilon_s + \epsilon_{\infty})}{\epsilon_s(\epsilon_{\infty} + 2)^2} = \frac{N_0 \mu^2}{3\epsilon_0 3KT} \quad (3)$$

Where ϵ_s and ϵ_{∞} are the static and high frequency permittivities, respectively, corresponding to particular relaxation process in the Cole-Cole diagrams.

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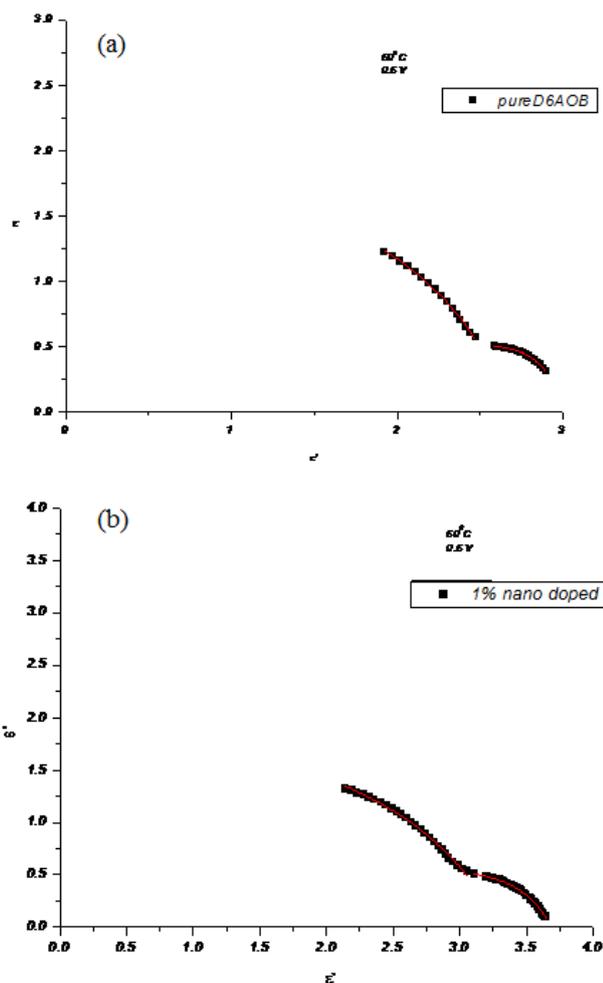


Fig. 3 Cole- Cole curves for homeotropic alignment of pure and ZONPs doped sample near the isotropic phase.

The Cole-Cole plots show the semi circle indicating to relaxation phenomenon. The one on lower frequency side is due to μ_1 while other on the higher side is for μ_2 . By using the help of equation 3 and Cole- Cole plot of figure 3, one can find the expression for μ_1 and μ_2 have been obtained. The values of increment of dielectric permittivity (ϵ) are obtained from the Cole-Cole plot of figure.3. Hence from figure 3 the angle $\beta = \tan^{-1}(\mu_2/\mu_1)$ can be calculated [20]. The angle β for molecules of pure D6AOB sample is found to be 64.5° which is in good agreement with the earlier reported value [12, 13]. The value of β for the molecules in the ZONPs doped LC suspension is found to be 75° . It means the angle β for the molecules in the doped sample has increased. In other words the resultant dipole moment of the LC molecule attains a new orientation with respect to their long molecular axis. Therefore it can be concluded that the ZONPs significantly influence the geometrical orientation of the D6AOB molecules in the suspension. In the light of eq. 2 we can say that on increasing the value of β , dielectric anisotropy of the doped sample is decreased with respect to the pure sample.

Further it is seen that $\epsilon_{||}$ increases gradually with decreasing temperature for all samples, which is due to the increasing nematic order [12]. Hence dielectric anisotropy $\Delta\epsilon (= \epsilon_{||} - \epsilon_{\perp})$ obtained from the values of dielectric permittivities below the

isotropic (I) to nematic(N) phase transition, was found to increase with decreasing temperature.

It is due to the contribution of the electronic polarizability to ϵ' which is greater in the direction along the molecular long axis than perpendicular to it. For D6AOB there is an additional permanent dipole moment which contributes slightly more in the perpendicular direction than in the parallel alignment. The decrease in dielectric anisotropy is caused by a decrease in the value of $\epsilon_{||}$ with increasing temperature, while the ϵ_{\perp} varies in an irregular manner. The decrease of $\epsilon_{||}$ in ZONPs doped sample results from the smaller distance between the molecules leading to an increased antiparallel correlation between the component of the dipole moment along the molecular axis. Consequently the effective dipole moment is reduced, causing a decrease in $\epsilon_{||}$. The absolute value of $\epsilon_{||}$ and ϵ_{\perp} of D6AOBs with weak dipole moment is much smaller than for LC with a strong dipole moment such as 5CB which have values 18.5 and 7.0 at room temperature for parallel and perpendicular component respectively [12,13].

In the ZONPs sample the effect of nano particle was enough to affect director in the phase, which prevent the alignment of the director in the field direction, hence in this case the value of $\epsilon_{||}$ obtained in close to the average value $(\epsilon_{||} + 2\epsilon_{\perp})/3$ as molecules would have deviated in their orientation around ZONPs. We have also observe the dielectric anisotropy with variation of different bias voltage as we are well aware that with the field induced reorientation of the pure LC director in a planar aligned cell the molecule orient themselves to the plan of the cell. An electric field applied perpendicular to the cell interacts with the dielectric anisotropy of LC system and forces the molecules with the positive dielectric anisotropy to align in the direction of the field, thereby achieving homeotropic alignment.

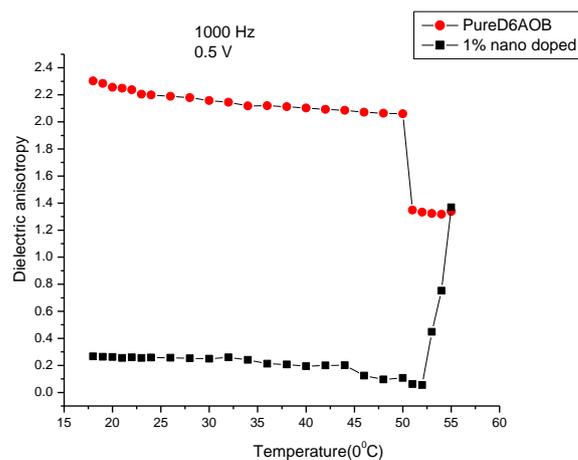


Fig. 4 Variation of dielectric anisotropy with temperature for both samples [12, 13]

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decrease in dielectric anisotropy is caused by a decrease in the value of ϵ_{\parallel} with increasing temperature, while the ϵ_{\perp} varies in an irregular manner. The decrease of ϵ_{\parallel} in ZONPs doped sample results from the smaller distance between the molecules leading to an increased antiparallel correlation between the component of the dipole moment along the molecular axis. Consequently the effective dipole moment is reduced, causing a decrease in ϵ_{\parallel} . The absolute value of ϵ_{\parallel} and ϵ_{\perp} of D6AOBs with weak dipole moment is much smaller than for LC with a strong dipole moment such as 5CB which have values 18.5 and 7.0 at room temperature for parallel and perpendicular component respectively [12,13].

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In an ideal homeotropic orientation, the molecule aligns themselves perpendicular to the cell plane. Sufficient field is needed to obtain a fully vertically aligned status. Above the threshold as we increase the voltage, the dipoles (in case of D6AOBs it makes an angle of 64.9° with that of the long molecular axis and in ZONPs the spontaneous polarisation is along the C-axis of the particles) try to align in the field direction [5]. At a particular voltage the dipole moment of the guest and the host get aligned in the field direction [21, 22]. But the long molecular axis of the guest and the host at this stage makes an angle from each other which will be the resultant of interaction of dipole moments of the guest and the host particles i.e. the molecules of D6AOBs and ZONPs are not completely aligned in parallel. At this stage the conclusion should be that on increasing the voltage gradually the anisotropy of the suspension might become constant above the threshold voltage as reported earlier [23]. The effect of ZONPs on the dielectric anisotropy of the suspension with variation of voltage can be seen on comparing the plot of $\epsilon_{\parallel} - \epsilon_{\perp}$ Vs V for pure D6AOBs and doped D6AOB as shown in figure 9. We see that the dielectric anisotropy of pure D6AOBs sample has not considerably changed on varying the voltage, i.e. it acquires the saturation value above the threshold voltage. But the anisotropy of doped sample decreases gradually on increasing the voltage. This nature of anisotropy can be explained on the basis of a new approach as following.

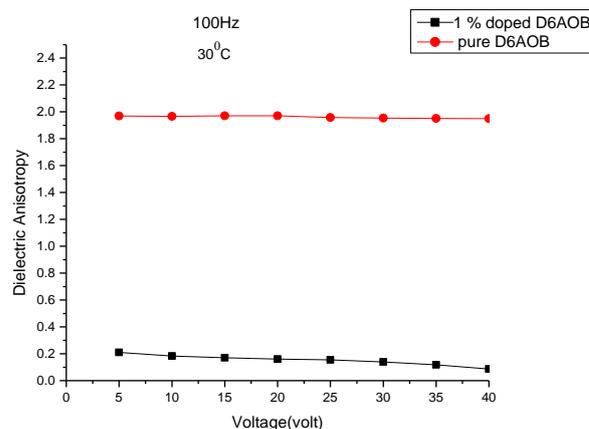
50 New approach

Recently a new phenomenon of superelastotropic elongation of carbon nano tube (CNT) aggregate has been observed in a super fluorinated nematic LC. The reported elongation in terms of actuation strain reaches up to 400 percent by an in plane actuation electric field of $5.67 \text{ V}(\mu\text{m}^{-1})$ at 60 Hz, and the original shape was restored by removal of the field. The resultant piezoelectric constant, defined as the ratio of the actuation strain to the actuation field was calculated to be several hundred times larger

than typical piezoelectric polymer accordingly. As a consequence, the carbon nano tube (CNT) aggregate resembled an elastomer substance with high expansion coefficient [24].

Since ZONPs show good piezoelectricity when they are subjected to an external electric field, the rod shape ZONPs may have similar behaviour as CNTs in the pure D6AOB sample. Hence in external field condition the ZONPs may change their shape. The slight shape change of the particles [in our case ZONPs] during applied electric field above the threshold cause a change in the stability of the surrounding liquid crystalline phase [25].

Therefore the liquid crystalline order is somewhat destroyed. This effect obviously causes the decrease in the anisotropy on increasing voltage above the threshold. Hence the hypothesis of isotropization [26], is found in our experimental results of anisotropy. Isotropization is a consequence of the disorder that is introduced by the guest particles in the liquid crystalline phase. The ZONPs network divides the LC molecules over domains, which in course disrupts the long range liquid crystalline order. This means that the structure, and consequently also the dynamics, will be driven towards a more isotropic one. One of the effects of the liquid crystalline order is a retardation of the rotation of short axis compared to the isotropic phase. If the order is disrupted, this rotation should become faster again, evolving in the direction of the isotropic value with increasing disorder [26, 27]. This piezoelectric effect of nanoparticles on the LC molecules provides a new way of research [28].



85 **Fig. 5** Variation of dielectric anisotropy with voltage



90 **Fig. 6** ZONPs (nano rods) in the nematic LC above threshold field

Conclusion

The results of dielectric studies performed for pure D6AOB nematic LC and ZONPs doped nematic LC allow us to note that:

- (1) The doped sample changes the sign of dielectric anisotropy before MHz region of frequency and variation of its value from +0.2 to -0.2 around the 1 MHz in the small frequency range. This can be useful for the design of dual addressing displays.
- (2) The angle (β) formed by the dipole moment with the long molecular axis could be estimated from the Cole-Cole plot of the pure D6AOB and doped D6AOB and with the help of Onsager theory at the temperature near the phase transition.
- (3) The angle β increases for the doped sample and hence the dielectric anisotropy for the doped sample decreases which provide a way to get the desired anisotropy of the system by doping a definite amount of nanoparticles.
- (4) The variation of anisotropy with temperature for both pure and doped D6AOB sample is same as reported by previous researchers i.e. on decreasing the temperature anisotropy increases due to increasing nematic order.
- (5) The anisotropy of the pure D6AOB sample almost remains constant with increasing the voltage however the anisotropy of the doped sample decreases with increasing the voltage. This decrease in dielectric anisotropy of the doped sample with increasing voltage could be explained on the basis of piezoelectric strain of the nano particles.

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Notes and References

¹Department of Physics, Govt. Vivekanand (P.G) College, Manendragarh, 497442 India

²Department of Chemistry, Govt. Nveen College Khadgawan, Chhattisgarh, India

³Department of Electronics and Communication, BIT Ranchi, Jharkhand, India

E-mail: kamalpandey27@gmail.com

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