

Comparative Study of Nanoparticle Doped Nematic Liquid Crystals

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Cite this article: J. Sci. Res. Adv. Vol. 1, No. 1, 2014, 13-17.

We have analyzed the influence of zinc oxide nanoparticles on the functional dielectric properties of nematic liquid crystal. In the present work we have done comparative dielectric study of nematic liquid crystals 5CB and D6AOB and its 1% wt/wt concentration with zinc oxide nanoparticles. The doping of the nanoparticles is found to affect all the electro-optic properties of nematic liquid crystal. In addition to this, the functional dielectric anisotropy of the doped samples takes another value. Here is an attempt to find the dielectric anisotropy and relaxation frequency for all samples. The increasing and decreasing of threshold voltage has also been discussed.

Introduction

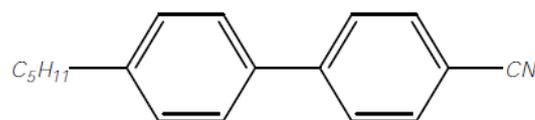
The Dispersions of nematic liquid crystals (LC) with nano particles like Pd, Ag, Ag/Pd, inorganic nano particles of MgO, and polymeric nano structures have been the subject of many studies since their introduction as a potential means for bistable liquid crystal displays [1-3]. However it turned out that the zinc oxide nano particles (ZONPs) are also useful in the studies of equilibrium conditions in the liquid crystalline systems [3,4].

Apart from calorimetric, NMR study and other techniques, dielectric spectroscopy can also investigate certain important untouched aspects of nanonematic suspension. The other and more important aspect of LC research involves selective chemical design of nematic molecule to enhance their electro optic performance [5-7]. It is felt useful to study the dynamics of liquid crystalline molecular dipoles in the vicinity of the isotropic to nematic (IN) transition, which provide the valuable information regarding the relaxation frequencies, relaxation strength, dielectric anisotropy and distribution parameter. The IN transition is accompanied by the breaking of isotropic, infinite, rotational symmetry with decreasing temperature is predicted to the weakly first order [8, 9]. Dielectric experimental studies of nematic LCs can provide information about the molecular arrangement, intermolecular interaction and the dynamics of reorientational motions. This information is useful in the design of a nematic device and more particularly for twisted nematic displays [10,11]. The ZONPs has attracted great interest in recent past. Due to its excellent chemical and physical properties ZONPs has a wide range of applications in piezoelectric transducers, photonic crystals, photo detectors, photodiodes, light emitting devices, transparent conductive films etc. [12]. The dispersion and alignment of ZONPs may be an important issue to improving mechanical, thermal, electrical and optical properties of host materials such as polymers and LCs. The ZONPs has the large band gap at room temperature (3.37 eV) [12,13]. It has the spontaneous polarization along of C- axis and having the wurtzite structure. The interaction between LC molecules and the ZONPs leads a number of changes in the properties of liquid crystalline phases [12-15].

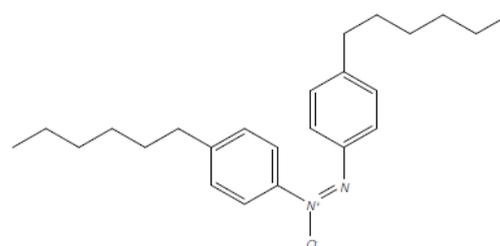
Experimental details

Materials

ZONPs doped LC suspension of a nematic LC host; 4, 4'-pentyl cyano biphenyl (5CB) and dihexyl azoxy benzene (D6AOB) have been used for the present investigations. The molecular structure and phase transition sequence of these nematics are given as below



4,4' pentyl cyano biphenyl (5CB)
Cr-----(22.5°C)----- nematic ---(35.3°C)-----isotropic



Cr-----(22°C)----- nematic ---(51°C)-----isotropic
4, 4'-di hexyl azoxy benzene (D6AOB)

Figure1 Molecular structure of LCs used for study (a) 5CB nematic with transition scheme (b) D6AOB nematic with transition scheme.

The 5CB is well-known LC used for our study [19]. It has the Cyano group at their one end, which makes it highly polar molecule. The alkyl chains on each side of the D6AOB molecules provide the added advantage that the deviation of the molecular long axis from the direction of the applied field is to be minimal.

The dipole moment in D6AOB has the magnitude of 1.70 D making an angle of 64.9° from the long molecular axis [20]. The host materials have been purchased from Flintron Laboratories U.S.A.

5 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 [12].

We have used planar as well as homeotropic alignment of LCs 10 for our dielectric studies. The sandwiched type (parallel plate capacitor) cells were made using two optically plane glass substrates coated with conducting ITO (Indium Tin Oxide) layers [ref].

15 Dielectric measurement

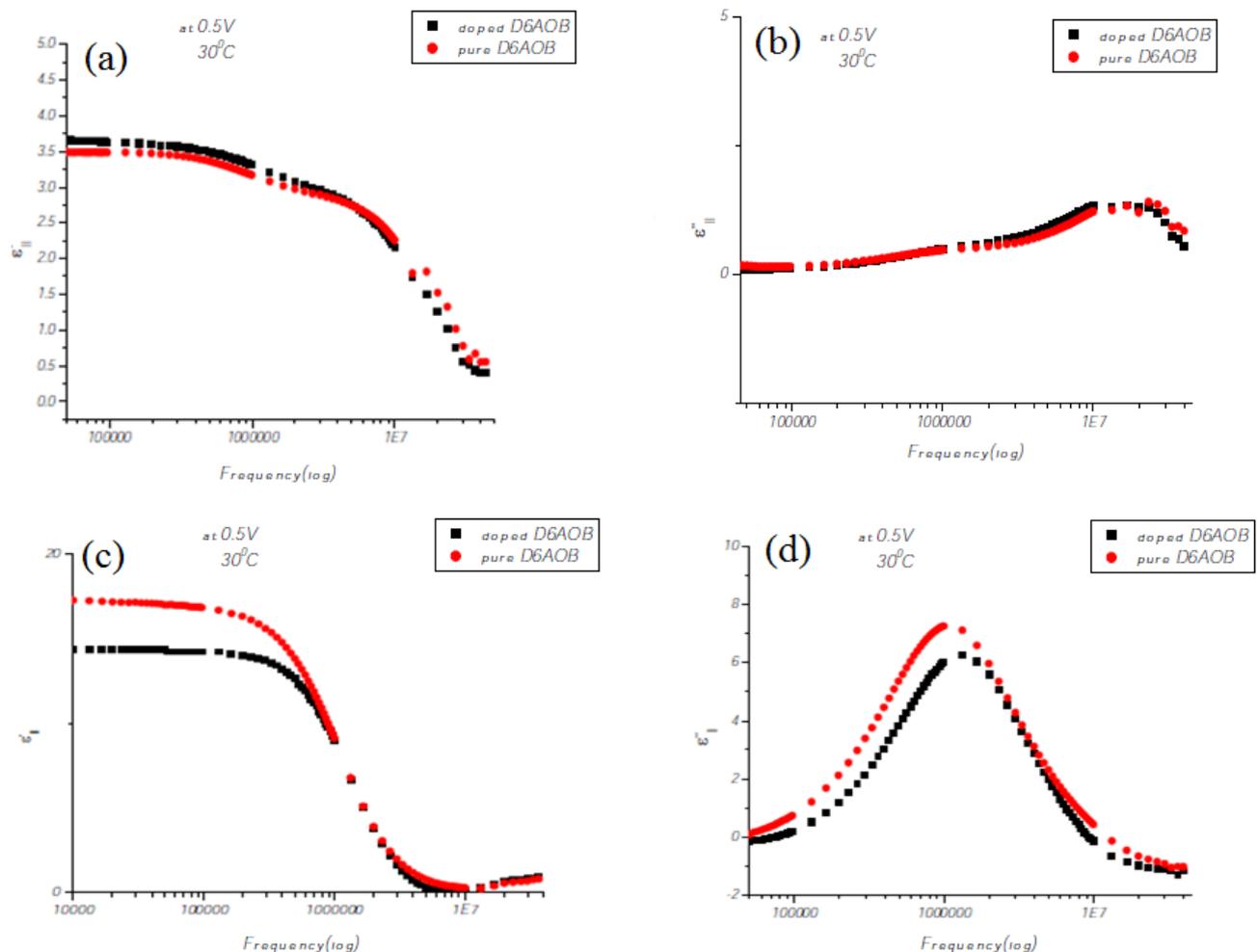
Dielectric measurements were carried out using a computer

controlled impedance Gain/Phase analyzer (HP 4194A) attached with a temperature controller in the frequency range 100 Hz to 40MHz.

20 The dielectric relaxation phenomena for both the samples in nematic phase have been examined using Cole- Cole relation. The Cole-Cole [24], 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 $\epsilon'(\infty)$ 25 is high frequency limit of the relative dielectric permittivity, $\omega(=2\pi f)$ is the angular frequency, τ is the relaxation time and α is the distribution parameter.



30 **Figure 2** Real and imaginary part of dielectric permittivity (ϵ' & ϵ'') as a function of frequency in homeotropic alignment for D6AOB (a & b) and 5CB (c & d) molecules in their bulk and doped form.

The low and high frequency deviations in dielectric data require 35 separating the real and imaginary part of the equation (1) one may get

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

and

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

(1b)

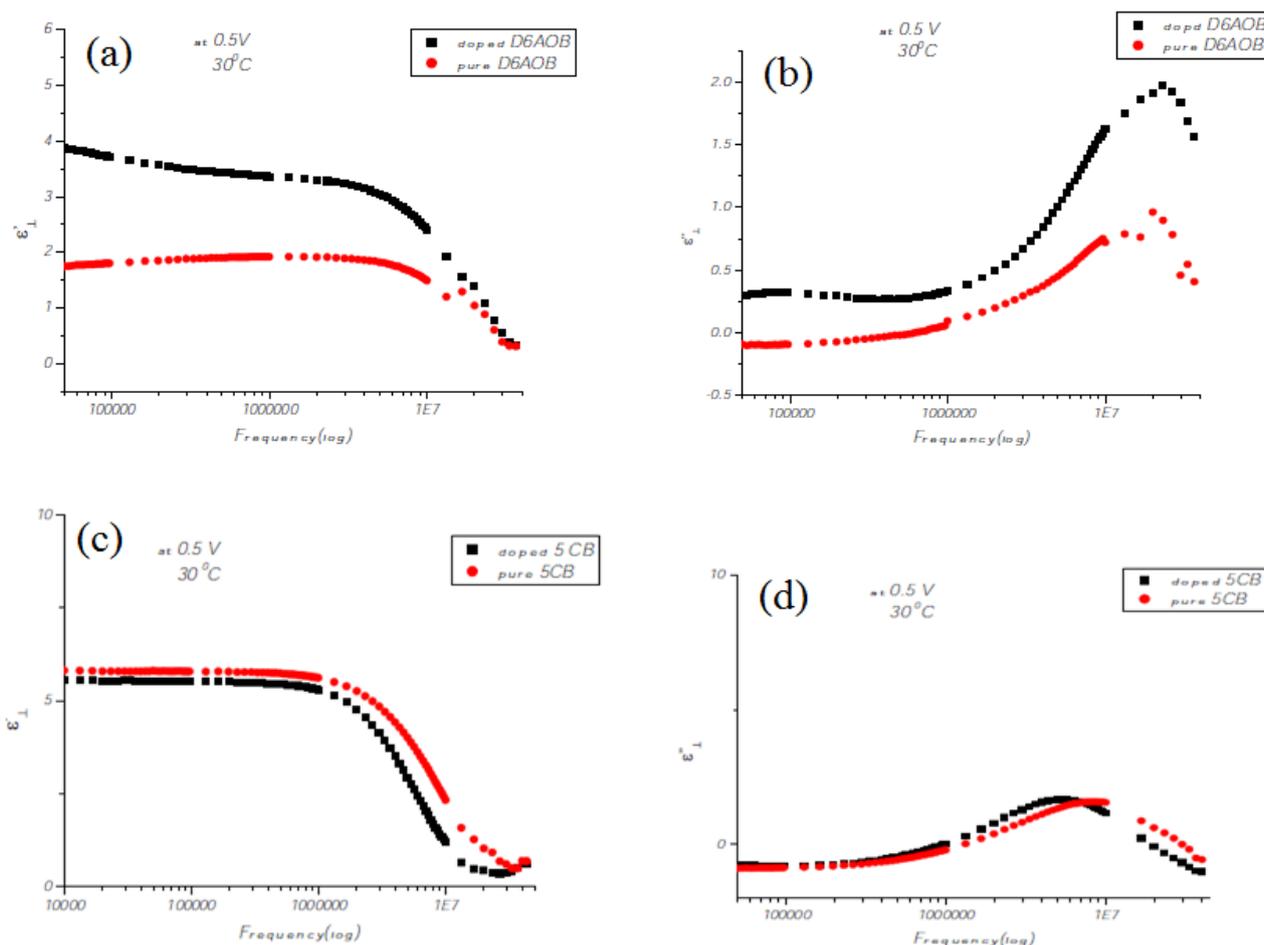
Here $\sigma(\text{dc})$ is the ionic conductance and ϵ_0 is the free space permittivity; k , A and m are the fitting parameters; α is the distribution parameter and ω is the angular frequency. The term $\epsilon'(\text{dc})/f^n$ and $\sigma(\text{dc})/\epsilon_0 2\pi f^k$ are added in the above equation 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. By the least square fitting of above equation into the experimental data we have removed the

low and high frequency errors [21-23].

Result and discussion

15 Dielectric permittivity

In order to study the influence of the ZONPs on the rotational motions of the molecules of the pure liquid crystal, dielectric relaxation spectra were obtained for D6AOB and 5CB in their bulk and 1 %wt/wt dispersed form. The real and imaginary part of dielectric permittivity (ϵ' & ϵ'') of D6AOB and 5CB were measured at 30°C, as a function of frequency for homeotropic orientation (electric field parallel to the molecular director) and planar orientation (electric field perpendicular to the molecular director) are shown in figure 2 and figure 3 respectively.



25 Figure 3 Real and imaginary part of dielectric permittivity (ϵ' & ϵ'') as a function of frequency in planar alignment for D6AOB (a & b) and 5CB (c & d) molecules in their bulk and doped form.

Homeotropic orientation

30 The frequency dependences of the dielectric permittivity for ZONPs dispersed D6AOB in the nematic phase for homeotropic alignment are shown in figure 2 (a & b), which gives typical relaxation spectra observed in nematic phases with homeotropic alignment. The strong dependence of frequencies of the processes corresponding to the rotations around short and long molecular

axis is known in general for LCs. In the D6AOB the molecular relaxation at the characteristic frequency 0.96 MHz is due to the rotation around short axis and is a slow process whereas the relaxation at the characteristic frequency above 10 MHz is due to the rotation of molecules around the long axis and is a fast process [25]. The ZONPs has little influences on the relaxation processes of D6AOB in doped sample. The both processes in bulk and ZONPs dispersed D6AOB are quite similar whereas the

5CB in their bulk and dispersed form has minor difference between the relaxation peaks at the same frequency. In comparison with 5CB it can be inferred that the strength of the dipole moments has small or may be no influence on the relaxation frequencies [16, 25-27]. The 5CB molecule in their bulk and dispersed form has no prominent relaxation around the short axis. The only process is that the molecular rotation around the long molecular axis is at the characteristic frequency of 0.99 MHz. This is due to the almost linear shape of 5CB molecule in which the angle between the long molecular axis and dipole moment is only 7.9° ; the major contribution of dipole moment is towards the long molecular axis [20, 25].

Planar Orientation:

The molecular relaxation spectra for planar orientation are shown in figure 3. In the case where the director is perpendicular to the field, no any process in the bulk D6AOB has observed. However there a major process could be observed in the GHz region [20, 25]. In the case of dispersed D6AOB a slow process seemed to have emerged with a maximum around 100 KHz as shown in figure 3(a) and 3 (b). We think there may exist a slow collective relaxation process due to the orientation of permanent dipoles at the ZONPs-LC interfaces. However it is difficult to exclude the possibility that the process could instead be due to the Maxwell-Wagner effect resulting from free ions and the network [20, 25-26].

In the case of 5CB in bulk and dispersed form, the typical relaxation spectra were obtained. It is observed that the fast process in bulk 5CB obtained at the characteristic frequency 9.3 MHz. In dispersed 5CB this process becomes slow and attaining the characteristic frequency 5.3MHz. In the case of 5CB dispersed with ZONPs the hindrance in rotation around the short axis is due to the higher viscosity in the surface layers, which is greater than the bulk viscosity. A cause of the higher viscosity may be preference of the dipole moment that is at the end of the

35 molecule which interacts with permanent dipole moment of the ZONPs. Thus preferential polar ordering can also exist at the surface with polar cyano group pointing towards the ZONPs. This process may be dynamic leading to a considerable slowing of the rotation of the molecule [25-27].

40 Dielectric Anisotropy

In order to study the frequency response of the nematic dipoles the dielectric anisotropy for both LCs in bulk and dispersed form has been plotted in figure 4. In the nematic phase both substances in bulk form exhibit a positive dielectric anisotropy $\Delta\epsilon = \epsilon_{||} - \epsilon_{\perp}$ in the large frequency range. The value of dielectric anisotropy for doped D6AOB and 5CB sample at MHz frequency range decreases significantly, suggesting that ZONPs affect the parallel and perpendicular component of dielectric permittivity ($\epsilon_{||}$ & ϵ_{\perp}). The 5CB sample in bulk and dispersed form shows the same trend of dielectric anisotropy versus frequency curve and in the MHz region both the graph overlap. This reflects the flat behavior of parallel and perpendicular component of dielectric permittivity in 5CB sample. However dielectric permittivity for doped D6AOB goes from positive to negative before the MHz region. We believe that the reason for the dielectric anisotropy of ZONPs dispersed D6AOB is attributed to the fact of nonlinear shape of D6AOB molecule and geometrical anisotropy of ZONPs. The geometrical anisotropy of ZONPs is not taken into account in the theory of dielectric properties of heterogeneous system. Hence the dispersion of the parallel component of the dielectric permittivity and a flat behavior of the perpendicular component over broad range of frequency is obtained. This effect enables the ZONPs dispersed D6AOB for effective dual addressing of the nematic LC displays. Based on this discussion it is seemed that the weakly polar LC may be more useful compared to highly polar LC when dispersed with ZONPs.

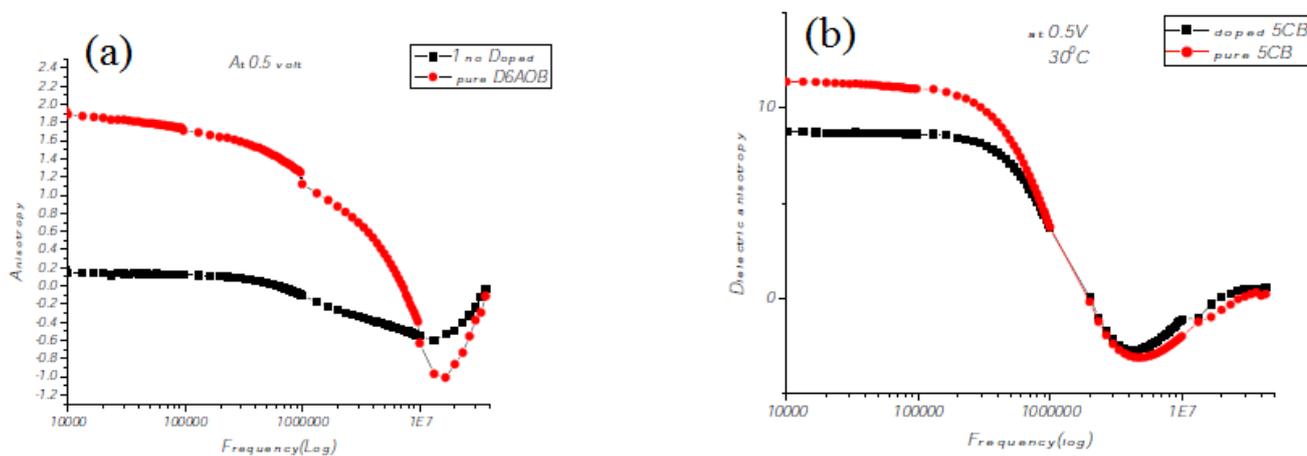


Figure 4 Behavior of dielectric anisotropy as a function of frequency for 5CB (a) and D6AOB (b) in their bulk and doped form.

Conclusion

The ZONPs doped D6AOB and 5 CB shows the qualitatively

different relaxation spectra in homeotropic and planar alignment. This is explained in terms of dipole moment contribution along the short and long molecular axis. The ZONPs doped D6AOB shows a new relaxation mode which is due to possibilities of slow collective relaxation process due to the orientation of permanent

dipoles at the ZONPs LC interfaces. The acceleration of D6AOB and 5CB molecules in ZONPs doped form is greater than bulk form. A dielectric anisotropy of D6AOB and 5CB in their bulk and doped form were studied. The ZONPs doped D6AOB is found useful in dual addressing displays.

Notes and References

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