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Dielectric and electro-optical study of ZnO nano rods doped ferroelectric liquid crystals

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Abstract Addition of Nano rods results change in the dielectric and electro-optical properties of pure Ferroelectric Liquid Crystal (FLC) considerably. The present study is devoted to characterize the dielectric and electro-optical parameters of the FLC nano rods composite system. The size of nano rods is usually much bigger than that of FLC molecules, therefore, when they are doped in different concentrations, in pure FLC, their volume fraction plays considerable role in deciding the molecular dynamics of the resultant composite system. For the lesser concentrations, the nano rods offer mechanical strength to system geometry while at higher concentration of nano rods, they offer additional constraints on the system. In present report both of these aspects have been analyzed and explained.

Introduction

Ferroelectric liquid crystals (FLCs) i.e., titled smectic phase built up by chiral molecules [1] are exciting class of materials having various applications in display and other electro optic devices because of their low operating voltage and fast response time [2]. Due to these properties FLCs show many advantages over the nematic liquid crystal. But most of these FLC based displays are black and white in nature and suffer from low contrast ratio and small viewing angle [3]. These problems of FLC's are the consequence of chevron geometry formation. Chevron appears when a planar anchored FLC cell is cooled from SmA phase to SmC phase [4].

To create the optical contrast in these systems basically two modes are used i.e., the birefringence mode [5] and the Guest host mode [6]. In the birefringence mode the phase delay between the two components of the polarized light is controlled by the application of electric field. This electric field controlled phase delay allows light of any particular wavelength (color) to transmit or block. One can get color display by using the birefringence mode but there are some drastic shortcomings associated with this mode [7]. The controllable color range of the display is limited to very narrow part of the visible light. Therefore, it is not possible to provide the natural color image. The most prominent problem with this mode is that the displayed color strongly depends upon the viewing angle.

To overcome these problems of the birefringence mode, the idea of Guest–Host mode was suggested by G. H. Heilmeier and L. A. Zanoni in 1968 which creates an optical contrast, large vision angle, and uniform color in the LC based display [8]. In this way the concept of doping of different materials in LCs was introduced by many researchers. In this context different materials like dyes, polymers etc. in LCs are found to affect the LC geometry and thus their physical properties.

Since the discovery of nano particles, it has drawn a huge interest in fundamental and applied research. There are sufficient evidences that these nano particles show distinct characteristics from the micro crystalline structure. There is no scientific field where the nano materials are not being investigated and explored to find the advantages of these materials in improving the desired characteristic.

Nano particles doped LCs has been widely investigated recently [9]. The nano particles, dispersed in FLCs, may affect FLC matrices due to strong director deformations

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and break the continuous rotational symmetry of the system. So this type of perturbation, produced by nano particles in LC matrix modifies almost all the properties of the LC system. This non-synthetic method to modify the properties of LCs by adding nano particles are much easier than the conventional chemical synthetic method and it has induced many modified dielectric and electro optic properties. In addition to this, some of the research groups have presented the effect on alignment of LC molecules due to the addition of nano particles [10, 11].

So, we made an attempt that the addition of nano structures in LC may result in an enhanced dielectric response. In the present work, 10E (ZnO + 10% Cu) nano rods are added in two different concentrations (i.e., 1% and 3%) with the pure FLC mixture Felix17/100 and results have been analyzed for dielectric and electro-optical properties under various conditions of temperature and frequency. It is found that the addition of these nano rods changes almost all the dielectric and electro-optical properties of pure FLC drastically. The present study is also expected to give the information about the interaction of nano rods with FLC molecules and their contributions to the relaxation mode.

Experimental procedure

Material

The investigated FLC material used in the present study is Felix 17/100 (Clariant Chemicals Co. Ltd.) and the phase sequence of the sample is Cr, SmC*, SmA, N*, Iso at −20 °C, 72 °C, 82 °C, and 95 °C. The basic parameters of this FLC material are given in Table 1. The nano rods doped sample of Felix 017/100 was prepared by dispersion of 10E nano rods in 1% and 3% wt%/wt concentration in the pure FLC sample and termed as mixture 1 and mixture 2.

10E nano rods, used in present study are ZnO doped with 10% of Cu. These nano rods are prepared by solvothermal method using ethanol as solvent. The whole preparation reaction is carried out in a high pressure autoclave. The average crystallite size of nano rods using Debye–Scherrer's equation was found 10 nm approximately. The SEM analysis of nano rods (i.e., Fig. 1) provides the information about their rod shape structure and diameter i.e., about 12–15 nm and length about 40–80 nm.

Table 1 Basic parameters of the ferroelectric liquid crystal Felix 17/100

Property	Temp. (°C)	Values
Spontaneous polarization	25	47 nC/cm^2
Rotational viscosity	25	116 mPas
Cone angle (2θ)	25	55.1°
Helical pitch in N*	85	18 μm
Optical anisotropy	30	0.172

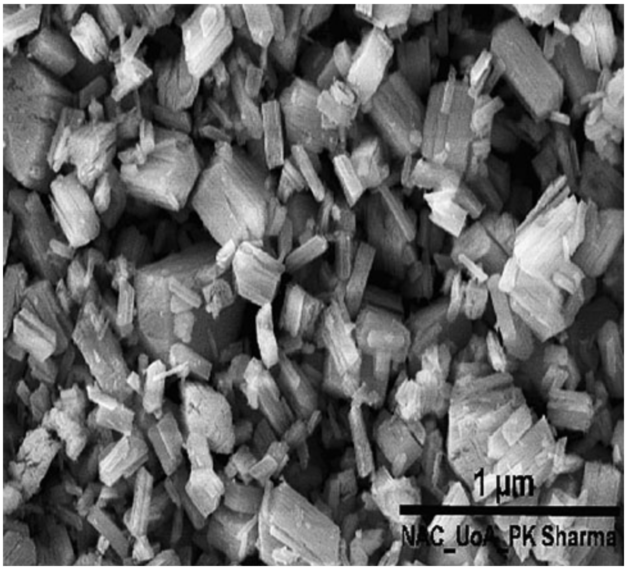

Fig. 1 Scanning Electron Microscope (SEM) image of nano rods (ZnO + 10% Cu) used for the present study

Heating the mixture of nano rods and FLC up to the isotropic transition temperature of the pure FLC and agitating the vial containing guest host mixture insures the uniform distribution of nano rods in the FLC sample.

Preparation for sample cell

The Dielectric study of nano rods doped FLC were conducted on planar geometry. The sand-witched type (capacitor) cells were made using two optically flat glass substrates coated with Indium tin oxide (ITO) layers. To obtain planar alignment, the conducting layer was treated with the adhesion promoter and coated with polymer nylon (6/6). After drying the polymer layer, substrates were rubbed unidirectionally. The substrates were then placed one over another to form a capacitor. The cell thickness was fixed by placing a Mylar spacer (6 μm in our case) in between and then sealed with UV sealant. The empty sample cells were calibrated using analytical reagent (AR) grade CCl_4 and benzene as standard references for dielectric study. The LC nano rods suspension was prepared by non synthetic chemical method in the weight ratio i.e., 1% and 3% concentration of nano rods in the pure FLC. The assembled cells were filled with the suspension and the pure FLC at a temperature higher than the isotropic temperature of the FLC by capillary method.

Dielectric measurement

The Dielectric measurements have been performed by computer controlled Impedance/Gain Analyzer (HP 4194 A) attached with a temperature controller in the frequency range 100 Hz to 10 MHz. The dielectric measurements have been carried out as a function of temperature by placing the sample on a computer controlled hot plate INSTEC (HCS-302).The temperature stability was better than ±0.1 °C with the measurements. Measurements in the higher frequency range have been limited to 10 MHz because of the dominating effect of finite resistance of ITO coated on glass plates and lead inductance [12–14].

The dielectric relaxation phenomenon of the pure and nano particle doped FLC have been analyzed using Cole–Cole relation-

$$\varepsilon^{*} = \varepsilon'(\infty) + \frac{\delta\varepsilon'_{\mathrm{GM}}}{1 + (i2\pi f\tau_{\mathrm{GM}})^{1-\alpha_{\mathrm{GM}}}} \tag{1}$$

where δ'_{GM} is the relaxation strength of the Goldstone mode and $\varepsilon'(\infty)$ is the high frequency limit of the dielectric permittivity data, f is the frequency and τ_{GM} is the relaxation time. As LCs are improper dielectrics the experimental data suffers from the two basic problems. The low and high frequency deviation in dielectric data and exceedingly require correction for low and high frequency values. On separating the real and imaginary part of Eq. 1 one may get

$$\varepsilon' = \varepsilon'(dc)f^{-n} + \varepsilon'(\infty) + \frac{\delta\varepsilon'_{\mathrm{GM}}[1 + (2\pi f\tau_{\mathrm{GM}})^{(1-\alpha_{\mathrm{GM}})}\sin(\alpha_{\mathrm{GM}}\pi/2)]}{1 + (2\pi f\tau_{\mathrm{GM}})^{2(1-\alpha_{\mathrm{GM}})} + 2(2\pi f\tau_{\mathrm{GM}})^{(1-\alpha_{\mathrm{GM}})}\sin(\alpha_{\mathrm{GM}}\pi/2)} \tag{2}$$

and

$$\varepsilon'' = \frac{\sigma(dc)}{\varepsilon_0 2\pi f^{k}} + \frac{\delta\varepsilon'_{\mathrm{GM}}(2\pi f\tau_{\mathrm{GM}})^{(1-\alpha_{\mathrm{GM}})}\cos(\alpha_{\mathrm{GM}}\pi/2)}{1 + (2\pi f\tau_{\mathrm{GM}})^{2(1-\alpha_{\mathrm{GM}})} + 2(2\pi f\tau_{\mathrm{GM}})^{(1-\alpha_{\mathrm{GM}})}\sin(\alpha_{\mathrm{GM}}\pi/2)} + Af^{m} \tag{3}$$

Here $\sigma(dc)$ is the dc ionic conductance, ε_o is the free space permittivity and f is the frequency while n, m and k are the fitting parameters. The terms $\varepsilon'(dc)f - n$ and $\sigma(dc)/\varepsilon_o 2\pi f^{k}$ are added in (2) & (3) for correcting the low frequency effect due to the electrode polarization capacitance and ionic conductance. The $Af\ m$ term is added in Eq. 3 for correcting the high frequency effect due to the ITO resistance and lead inductance [15, 16].The other abbreviations are same as given for Eq. 1. The experimental data have been fitted in these equations and corrected for low and high frequency values [17].

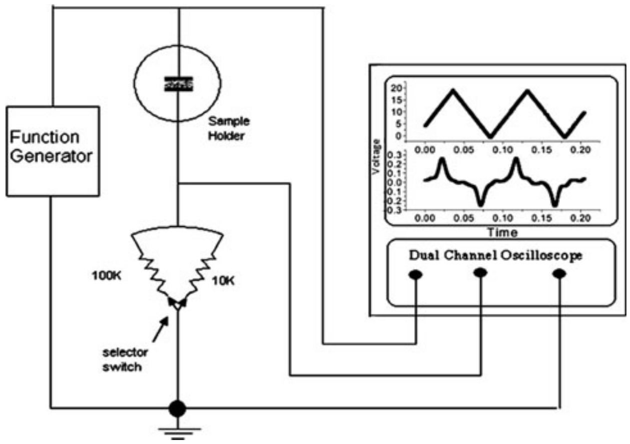

Fig. 2 Experimental set up for the measurement of spontaneous polarization for both the pure and doped sample

Electro-optical measurement

To measure the spontaneous polarization of the pure and the doped system, polarization reversal current method has been used [12–14]. The complete experimental arrangement for this measurement is given in Fig. 2.

Results and discussion

The morphology of small particles is obtained by scanning electron microscope (SEM) technique. Figure 1 is SEM image of 10E (ZnO + 10% Cu) nano rods. The dimensions of these nano rods suggest that doping of these nano rods would draw considerable effect on the properties of the pure FLC and offer many advance features for different applications.

The temperature dependence of dielectric permittivity of the pure and the nano rods doped FLC mixtures at 133 Hz has been shown in Fig. 3. The dielectric permittivity increases in SmC* phase smoothly with temperature and shows a maximum value just before SmC* to SmA phase transition temperature. This maximum value of dielectric permittivity indicates maximum strength of the helix in SmC* phase and on further increment in the temperature causes a sharp decrease in dielectric permittivity [18]. This abrupt fall in dielectric permittivity is due to the helix unwinding which starts just after showing maximum value of dielectric permittivity in SmC* phase [19–21].

The thermal behavior of dielectric permittivity observed for the nano rods doped FLC is similar to the pure FLC. An increase in the values of dielectric permittivity for mixture 1 and mixture 2 has been observed than the pure FLC mixture. The 1% and 3 wt%/wt concentration of nano rods is small but the size of nano rods is much bigger than the dimension of the LC matrix. Thus, these small

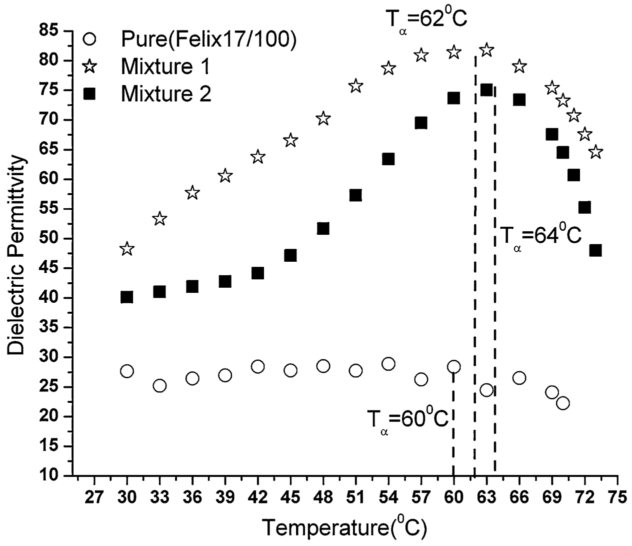

Fig. 3 Variation of dielectric permittivity with temperature at 133 Hz for pure and nano rod doped FLC Felix 17/100

concentrations of nano rods offer considerable change in all physical properties of the pure FLC.

The dielectric permittivity increases at higher temperatures for the nano-doped FLCs but the temperature dependence is not as that as for pure FLCs. It shows some sudden jump near the 43 °C. For mixture 1 this behavior can be neglected but for the higher concentration, i.e., mixture 2, it is significant. The sudden jump at 43 °C for mixture 2 can be explained by the semiconducting property of ZnO nano rods. Due to semiconducting nature of these nano rods, break down occurs at this temperature and a sudden change in the value of dielectric permittivity is observed. Pure FLC suffers from zig-zag defects i.e., chevron geometry. This zig-zag defect causes a reduction in the net dielectric contributions. After the addition of nano rods in the pure FLC sample, nano rods try to fit themselves in the geometry of the system which results in a decrement in the density of zig-zag defect. At higher concentrations, nano rods produce the hindrance in the molecular dynamics due to which net dielectric contribution is decreased. This different characteristics of relative permittivity suggest that nano rods are disturbing the pure FLC geometry that is considerable at higher concentrations. When nano rods are added to the pure FLC matrix the intrinsic FLC and surface interactions compel Nana rods to align them along the director. Therefore, dipole moment of the nano rods supports the dipole moment of the FLC molecules that can be attributed to the increment in the values of the dielectric permittivity. At the same time the size of nano rods are around 40–80 nm, therefore it can penetrate two adjacent smectic layers. This penetration will offer hindrance to the molecular dynamics of pure FLC and may be the reason for the different temperature dependence near 43 °C. In addition to these two major facts, one more thing that needs proper attention is piezoelectric properties of nano rods. This has been discussed in the next part of the article.

Another information from Fig. 3 that needs careful analysis is the temperature (T_α) at which relative permittivity is maximum in SmC* phase. From the figure it has been noticed that T_α for pure FLC is 60 °C and for mixture 1 and Mixture 2 it is 62 °C and 64 °C respectively. As T_α indicates the maximum strength of the helix, therefore from higher value of T_α for doped FLC system it can be concluded that the helix strengthens with the addition of the nano rods.

Figure 4 shows the absorption curves at temperature 36 °C in SmC* phase for pure and nano rods doped FLCs. The relaxation phenomenon of the FLC with a planar alignment is due to the collective dielectric processes such as Goldstone mode and soft mode [22]. The Goldstone mode dominates over the SmC* phase, whereas the Soft mode appears at the higher frequencies near the SmC*-SmA phase transition temperature [23]. From the figure it is clear that the relaxation band appears in low frequency region for all the systems and it is none other than Goldstone mode of relaxation which arises due to phase fluctuations of FLC molecules (ϕ fluctuations). The relaxation band of the Goldstone mode shifts for the nano rods doped FLC system in comparison to the pure FLC. The magnitude of dielectric loss for mixture 1 and mixture 2 is greater than that of the pure FLC mixture. In addition to this, for the doped system having lesser concentration of the nano rods (i.e., for mixture 1), the relaxation band shifts toward lower frequency range and for the mixture 2 of concentration it shift toward lower frequency side but lesser than mixture 1.

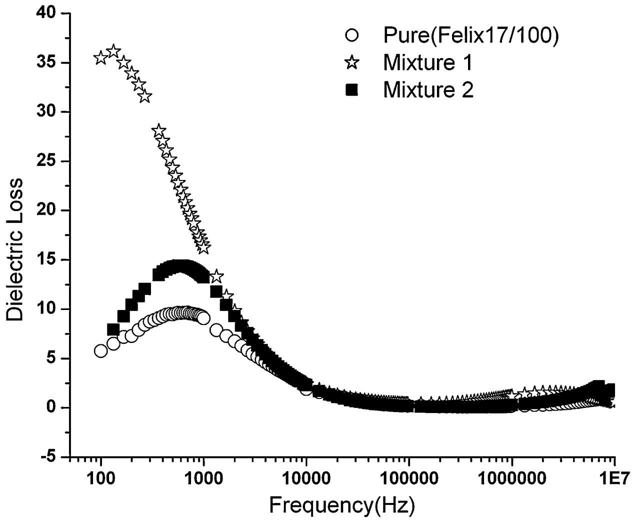

Fig. 4 Variation of dielectric loss with frequency for pure and nano rod doped FLC Felix 17/100

The plot between relaxation frequency of the Goldstone relaxation mode and temperature is shown in Fig. 5. It is clear from the Fig. 5 that the relaxation frequency for mixture 1 is almost temperature independent in the SmC* phase but increases sharply near SmC* to SmA phase transition temperature. This nature of relaxation frequency curve can be explained by Landau model

$$f_G = \frac{\Gamma K_3 q^2}{2\pi} \quad (4)$$

where, q is the wave vector of helix, K_3 is the twist elastic constant and Γ represents the inverse of rotational viscosity [24]. Relaxation frequency is inversely proportional with pitch of the helix which may change with the addition of nano rods. A decrement in the value of relaxation frequency for mixture 1 is observed. It is observed that for mixture 2, relaxation frequency is higher than the mixture 1 but still it is smaller than the relaxation frequency of the pure FLCs. As relaxation frequency depends upon q, K_3, and Γ, these may change with the addition of nano rods. With the high electric field of chosen experimental conditions, i.e., also holds for display, K_3 is negligible, hence only q and Γ are responsible for the changes produced in f_G. The effect of nano rods on q of pure FLC has already been discussed and the rotational viscosity will be discussed later.

Addition of nano rods in the pure FLC mixture causes the redistribution of the intermolecular interaction energies; hence many other properties are also changed. In the present study a clear change has been noticed for all properties, like relaxation strength, distribution parameter etc. related to the Goldstone mode for the doped system. The continuous distribution of relaxation phenomenon and above-mentioned properties has been studied in the light of Cole–Cole relation given by Eq. 1.

Figure 6 represents the Cole–Cole plots of the Pure and the doped system. The black open legends show the experimental data while the solid line represents the best theoretical fit in experimental data. It is clear from the figure that relaxation process of the samples is only due to the one relaxation mode which arises in low frequency regime i.e., Goldstone mode.

Relaxation strength of the Goldstone mode for both the pure and the nano rods doped FLC samples have been evaluated by fitting Cole–Cole equation in experimental data [25]. The variation of relaxation strength as a function of temperature is shown in Fig. 7 for both the pure and the nano rods doped FLC sample. A significant change in relaxation strength is observed for the nano rods doped system. The value of relaxation strength increases with increase in temperature and sharply decreases near the SmC* to SmA phase transition temperature. The relaxation strength can be explained theoretically with the help of the equation given below

$$\Delta\varepsilon_G = \frac{1}{2K_3\varepsilon_0}\left(\frac{P_s}{q\sin\theta}\right)^2 \quad (5)$$

where K_3 is the twist elastic constant, P_s is the spontaneous polarization and q is the wave vector of helix while θ represent tilt angle.

The Goldstone mode relaxation strength for mixture 1 and mixture 2 is greater than that of the pure FLC mixture. This increase in relaxation strength for mixture 1 and mixture 2 can be explained by the supportive nature of dipole moment of the nano rods with the dipole moment of the pure FLC molecules. The nature of relaxation strength

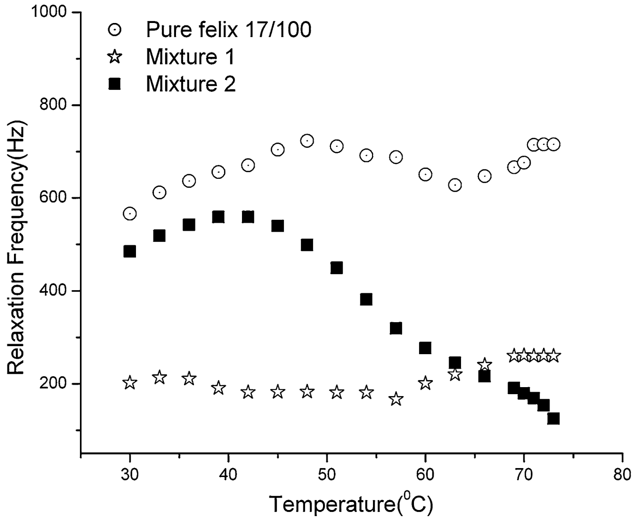

Fig. 5 Temperature dependence of the relaxation frequency for pure and nano rod doped FLC Felix 17/100

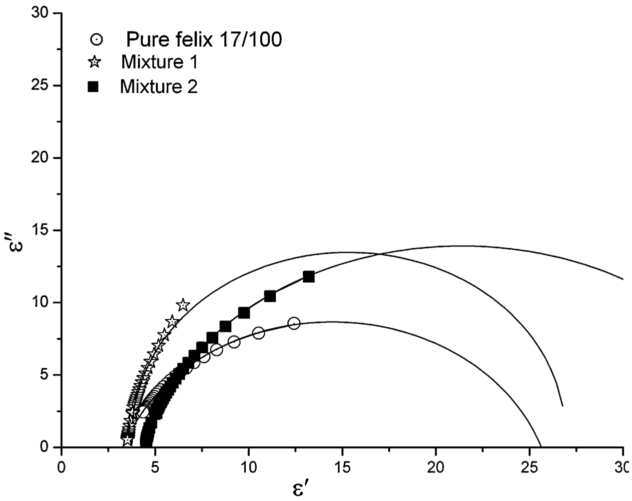

Fig. 6 Cole–Cole plots for pure and nano rod doped FLC Felix 17/100. The black open legends show the experimental data while the solid line represents the best theoretical fit in experimental data

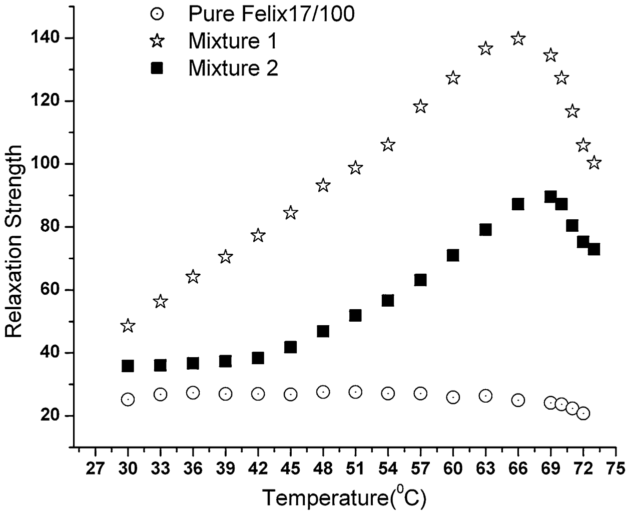

Fig. 7 Temperature dependence of the relaxation strength for pure and nano rod doped FLC Felix 17/100

of the pure and the nano rods doped system is in agreement with that of the dielectric permittivity.

Figure 8 shows the temperature dependence of distribution parameter (α). The distribution parameter of the pure FLC mixture increases at higher temperature. The smaller value of distribution parameter within the range of the SmC* phase temperature for the pure FLC mixture clearly indicates that Goldstone mode predominates over the soft mode in the SmC* phase [26]. The distribution parameter is reduced for the nano rods doped FLC systems (mixture 1 and mixture 2) which suggests that after doping of the nano rods the nature of relaxation phenomenon gets closer to Debye type of relaxation phenomenon. This indicates that for the nano rods doped systems Goldstone mode is stronger than the pure FLC.

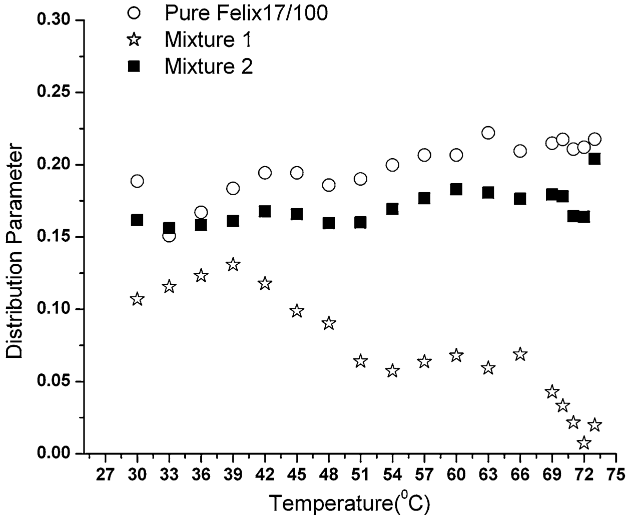

Fig. 8 Variation of distribution parameter with temperature for pure and nano rod doped FLC Felix 17/100

The detailed analysis of spontaneous polarization and rotational viscosity including tilt angle has been studied by electro-optical measurement. The variation of spontaneous polarization, tilt angle, and rotational viscosity for the pure and the nano rods doped FLC sample is shown in Fig. 9a, b, and c, respectively. The measurement of spontaneous polarization has been taken at 20 V peak to peak. At 35 °C the spontaneous polarization for mixture 1 is found lesser than the pure FLC mixture. For mixture 2, it is greater than mixture 1 but still less than the pure FLC mixture. The higher value of spontaneous polarization for mixture 2 is due to the piezoelectricity of the nano rods in mixture 2. This nature is also supported by the nature of relaxation frequency in which relaxation frequency for mixture 1 is less than the pure FLC mixture. For mixture 2 the relaxation frequency is greater than mixture 1 but shows decrement with that of the pure FLC mixture. The piezoelectricity also contributes for mixture 1 but it does not add any significant contribution. The variation in the rotational viscosity for mixture 1 decreases than the pure FLC sample but for mixture 2, rotational viscosity exceeds than that of the pure FLC. This is due to the higher concentration of nano rods. But for lesser concentration, the reduction in rotational viscosity is due to the decrease in the tilt angle of mixture 1. [13, 15] Tilt angle, the primary and preferred order parameter for SmC* phase, for mixture 1 decreases with the addition of nano rods in pure FLC, while for mixture 2, it increases in comparison to the pure FLC sample. This decrease in angle of tilt for mixture 1 is due to the interaction between FLC molecules in the presence of nano rods but this interaction becomes weaker for mixture 2, where interaction between nano rods and FLC molecules takes place and results in an increase in the tilt angle. With the help of Eqs. 4 and 5, we can show a relation between tilt angle and rotational viscosity as

$$\gamma_G = \frac{1}{4\pi\varepsilon_0}\frac{1}{\Delta\varepsilon_G f_G}\left(\frac{P_s}{q\sin\theta}\right)^2 \qquad (6)$$

where, symbols have their usual meanings.

For the mixture with lesser concentration (i.e. mixture 1) of nano rods in pure FLC geometry, the composite system does not follow the above relation due to small perturbation in FLC matrix but for mixture 2, composite system shows usual nature of rotational viscosity and tilt angle according to the above relation.

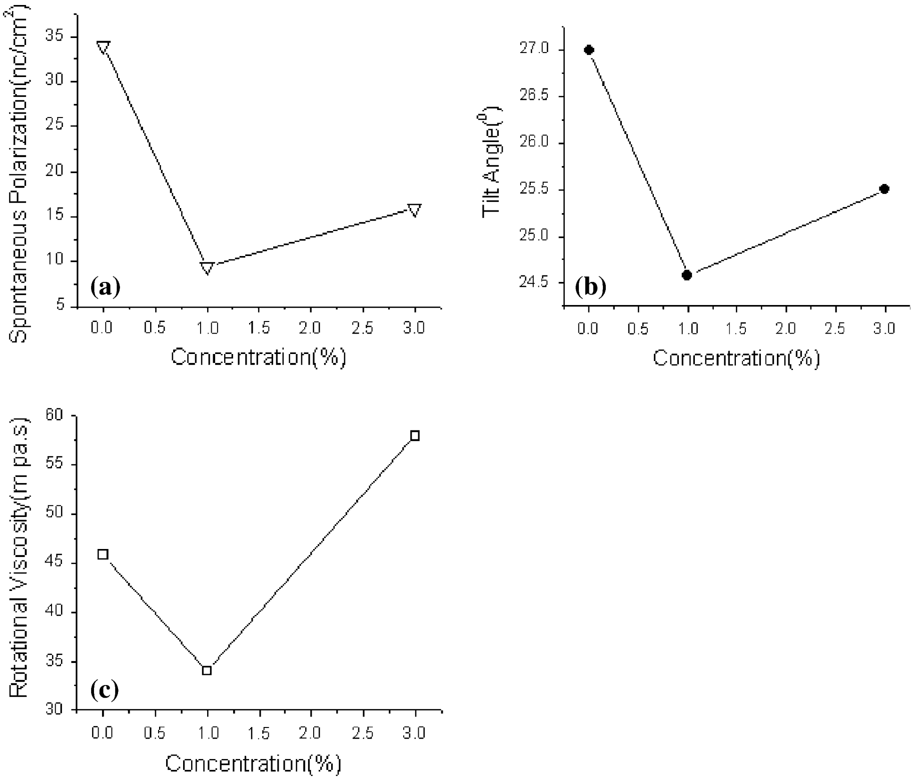

Fig. 9 Variation of different electro-optical parameters at 35 °C for the both pure and nano rod doped FLC nano rod Felix 17/100. (**a**) *open inverse triangle* represents the change in spontaneous polarization, (**b**) *filled circle* represents the change in tilt angle and (**c**) *open square* represents the change in rotational viscosity at different concentrations

Conclusions

The results of the present study can be summarized as follows:

1. The observation of variation in relative permittivity, relaxation frequency and spontaneous polarization depends upon the concentration of nano rods in the pure FLC sample.
2. Shift in the values of the T_{α} for doped FLCs confirms that the helical structure of pure FLCs changes with the addition of nano rods. This trend also confirms that the helix is stronger for the nano-doped FLC than the pure FLC.
3. Decrease in the value of distribution parameter for the nano rods doped FLC sample suggests that goldstone relaxation mode becomes stronger after the addition of the nano rods in the pure FLC matrix.
4. This complete behavior of all the properties can be attributed to three facts. First, size of nano rods due to which it may penetrate two or more smectic layers. Second, the piezoelectric property of the nano rods that contributes significantly to the FLC parameters. The last but not the least, the interaction between the nano rods and FLC geometry causes change in the helical pitch, consequently all the vital properties show considerable change.

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