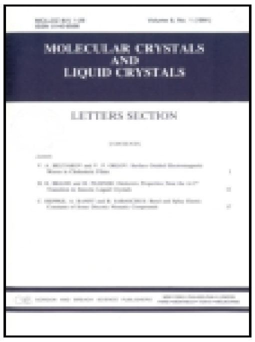

Molecular Crystals and Liquid Crystals

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On the dipole–dipole correlation and dielectric anisotropy of some N(4-N-alkyloxy benzylidene)4′-N-alkylaniline compounds doped with silver nanoparticles

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ABSTRACT
Dielectric study of the compounds N(4-n-heptyloxy benzylidene)4′-n-butylaniline and N(4-n-heptyloxy benzylidene)4′-n-hexylaniline at low frequency region (1 kHz–1 MHz) is performed using LCR meter (Agilent 4284 A). A qualitative interpretation in terms of dipole–dipole correlation for both the parallel and the perpendicular components of the dipole moment is given. Further study on the change in the dielectric permittivity and the dielectric anisotropy is made by doping the two compounds separately with dodecanethiol capped silver nanoparticles (0.25% by weight). The molecular positional ordering and relative smectic layer distance influences the change of degree (or type) of dipole–dipole pairing.

KEYWORDS
Dielectric anisotropy; dielectric permittivity; liquid crystals; silver nanoparticles

1. Introduction

Liquid crystals (LCs) are useful one- and two-dimensional fluids with state lying between the solid (crystal) and the liquid. The properties of LC are related mainly to its anisotropic geometrical structure [1] and additional dielectric properties are due to the presence of dipoles on it. The dielectric properties of simple nematic LC could be successfully studied using Maier and Meier formula [2] but for other smectic phases, modified theory based on extension of Kirkwood–Frohlich equation [3,4] and dipole–dipole correlation [5,6] are used. Later, Benguigui extended the approach of using dipole–dipole correlation and developed a theory [7] that could explain the dielectric anisotropy of liquid crystals showing smectic (Sm A, Sm B, and Sm C) phases. From the theory developed by him, the tendency for parallel components of the dipole moment to form antiparallel dipole ordering and for the perpendicular component to form parallel ordering was implicit. He used 5O.7 and 5O.8, which were negative dielectric anisotropic materials, for verifying the theory in a later work [8]. However, work done by Padmajarani et al. [9] on higher members of the same *n*O.*m* (*n* and *m* being the number of carbon atoms) compounds has shown results quite different from those of the lower members, used by Benguigui. For example, the permittivity value for homeotropic alignment increased with the decrease in temperature for the higher member while it decreased with

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decrease in temperature for the lower member. It shows the complexity in the dielectric properties of these compounds. So, we choose the compounds, N(4-n-heptyloxy benzylidene) 4′-n-butylaniline (7O.4) and N(4-n-heptyloxy benzylidene)4′-n-hexylaniline (7O.6), which have a dipole moment larger in comparison to that used by Benguigui but smaller to that used by Padmajarani et al. The compounds so chosen are rich in showing smectic polymorphism and have the phase sequence: Cr–Sm G–Sm C–Sm A–N–Iso for 7O.4 and Cr–Sm G–Sm F–Sm C–Sm A–Iso for 7O.6, respectively. First, a qualitative investigation for the type of dipole–dipole correlation in the different smectic phases of the compounds is made. In the course of study there is an indication of parallel dipole–dipole correlation for the parallel as well as the perpendicular components of dipole moment. This new finding could explain qualitatively the observed dielectric behavior of the higher homolog of this *n*O.*m* compounds. Also there appear a possible relation between the relative distance of the smectic layers and the type of dipole–dipole correlation. In order to enhance our understanding on the relative role of dipole orientation, we choose to dope the compounds with dodecanethiol capped silver nanoparticles (SNPs) in small amount and explore any change in the dielectric properties. It may be noted that -doping nanoparticles in LC has become a fascinating and interesting activity in recent works for enhancing the properties of the LCs and to compete with other rival materials. For example, suspending ferroelectric nanoparticles in a nematic liquid crystal host were found to enhance the dielectric anisotropy of the liquid crystal [10,11]; doping with MgO and SiO_2 nanoparticles has also been reported to decrease the threshold voltage of the nematic liquid crystal [12]. Enhancement of photoluminescence of nematic liquid crystal doped with silver nanoparticles [13] and ferroelectric liquid crystals doped with gold nanoparticles [14] has also been reported. But in our study, we focus on the effect of the SNPs and a qualitative understanding of the mechanism is attempted. However, it is not possible to separate the individual contribution of the capping layer or the size of nanoparticles, as we have used only dodecanethiol capped SNPs of 5–15 nm size. So, the effects due to SNPs mean the combined effect as referred here.

2. Experimental section

The liquid crystalline compounds 7O.4 and 7O.6 were prepared following a standard procedure given in the literature [15]. SNPs capped with dodecanethiol, purchased from Sigma-Aldrich (Product No. 667838, particle size 5–15 nm; Sigma-Aldrich India, Karnataka), were used to dope the compounds. The two compounds were separately doped with SNPs in 0.25% (by weight). The mixture was sonicated for 1 hr to obtain a uniform dispersion and the hexane present in the mixture sample was allowed to evaporate completely. Thus, we have four types of samples—pure 7O.4, pure 7O.6, doped 7O.4 (with SNPs in 0.25% by weight), and doped 7O.6 (with SNPs in 0.25% by weight). Four similar cells for homeotropic alignment were prepared by using highly conducting indium tin oxide (ITO) coated optically flat glass substrates as electrodes. First, the glass plates were thoroughly cleaned with soap solution followed by deionized water and acetone; then they were treated with high concentration of cetyltrimethyl ammonium bromide (CTAB) solution (6.8 mM L^{-1}) to get homeotropic alignment. Mylar spacer of 25 μm was used for maintaining cell gap. Following the method given in literature [16], another four similar cells were prepared for planar alignment by using low concentration of CTAB solution (0.254 μM L^{-1}).

Next, the empty cells were calibrated using air and benzene. Two cells—one for homeotropic alignment and the other for planar alignment—were taken and filled with pure 7O.4 sample at isotropic temperature. Similarly, two different types of cells (one for

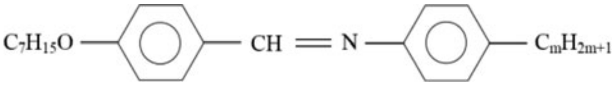

Figure 1. Molecular structure of 7O.*m* ($m = 4$ for 7O.4 and $m = 6$ for 7O.6).

homeotropic alignment and other for planar alignment) filled with each of the remaining three samples were made. All the dielectric measurements were made with LCR meter (Agilent 4284 A) in the frequency range of 1 kHz–1 MHz.

3. Results and discussion

The molecular structures of 7O.4 and 7O.6 are shown in Fig. 1. The transmission electron microscopy (TEM, Model JEOL JEM 2100) picture of the dispersed SNPs in the LC sample 7O.4 (representative) is shown in Fig. 2. The phase sequence and transition temperature are shown in Table 1. The transition temperature obtained from Differential Scanning Calorimetry (DSC) and Polarizing Thermal Microscopy (PTM) are in good agreement with literature values.

3.1. *Pure 7O.4 and Pure 7O.6*

The temperature variation of the static permittivity for the pure 7O.4 sample and the doped 7O.4 sample is shown in Figs. 3 and 4. Figures 5 and 6 are the magnified version. For the pure 7O.4 sample, the variation of the static permittivity with temperature clearly indicates the contribution of dipole moments in the temperature range studied. When the temperature is decreased, the permittivity value corresponding to homeotropic alignment increases through all the liquid crystalline phases while the permittivity value corresponding to planar alignment increases till the Sm G–Sm C transition temperature ($T = 62.1$ °C) and below this

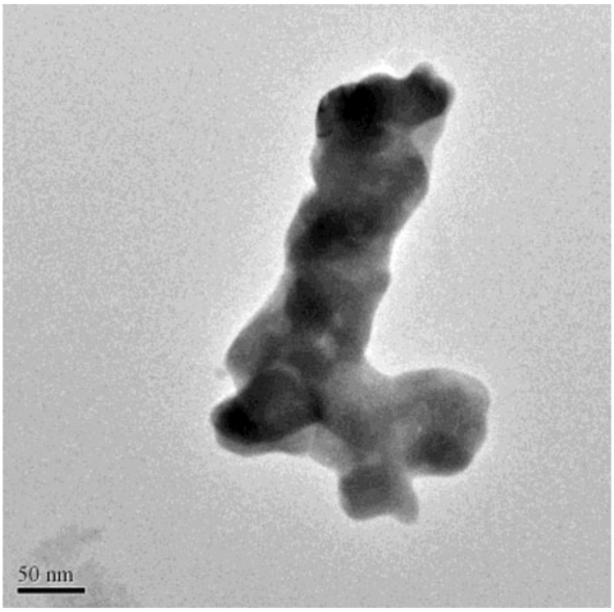

Figure 2. TEM picture (taken with Model JEOL JEM 2100) of dispersed SNPs in 7O.4 sample.

Table 1. Phase transition temperatures (in degree celcius) of 7O.4 (pure and doped) and 7O.6 (pure and doped).

Phase transition → sample ↓	SmG-SmF	SmG-SmC/ SmF-SmC	SmC-SmA	SmA-N	N-Iso/ Sm A-Iso
Pure 7O.4	–	62.1	64.1	72	74.1
Doped 7O.4	–	61.1	64.0	71.6	73.9
Pure 7O.6	55	66	69	–	81
Doped 7O.6	53.9	65.5	68.9	–	81

temperature (in the Sm G phase), one may observe the permittivity value for planar alignment showing anomalous variation with temperature. As the importance of dipole–dipole interaction in dielectric permittivity has been demonstrated [17,18], the observed variation of static permittivity with temperature may be interpreted by the behavior of dipole–dipole correlation. In the isotropic phase of pure 7O.4 sample, isotropic permittivity decreases with the increase in temperature. Such type of behavior may also be seen in the other members of the same *n*O.*m* homologs [8,9,19]. This could be due to the existence of pre-transition parallel dipole–dipole correlation effect in the isotropic phase and the strength (or degree) of parallel dipole–dipole correlation decreasing with the increase of temperature in this phase. Generally, the increase of average permittivity with decrease in temperature is considered as showing normal behavior [20]. This could be due to parallel dipole pairing effect. The parallel dipole pairing, which is unfavorable at normal condition, may be favored due to temperature [21] and other factors.

It was also explained that antiparallel short range correlations exist for those compounds [22] where the average dielectric permittivity shows a discontinuous jump with values lower than the extrapolated permittivity from isotropic phase. The observed increase in the permittivity with the decrease of temperature for both of the alignments (homeotropic and planar) can be explained (qualitatively) if the parallel dipole–dipole correlation type exists for the parallel as well as the perpendicular components of the dipole. However, the type and the degree of dipole–dipole correlation may differ significantly for the two components of dipole in the Sm G phase. This may imply the importance of molecular positional ordering in this phase affecting the dipole–dipole correlation. Similar observations [23], where the average

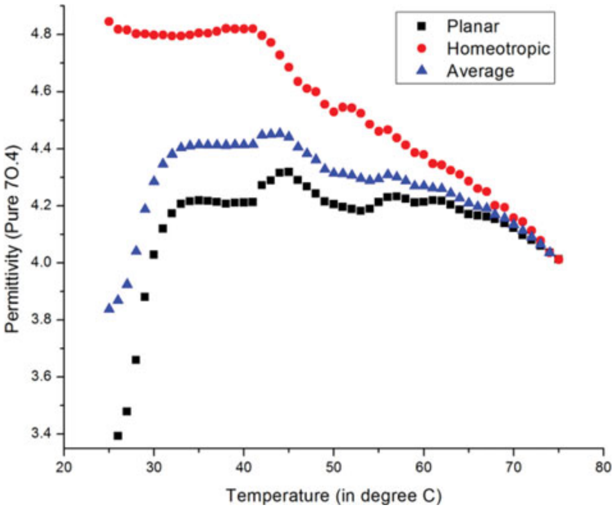

Figure 3. Static permittivity versus temperature for pure 7O.4 sample.

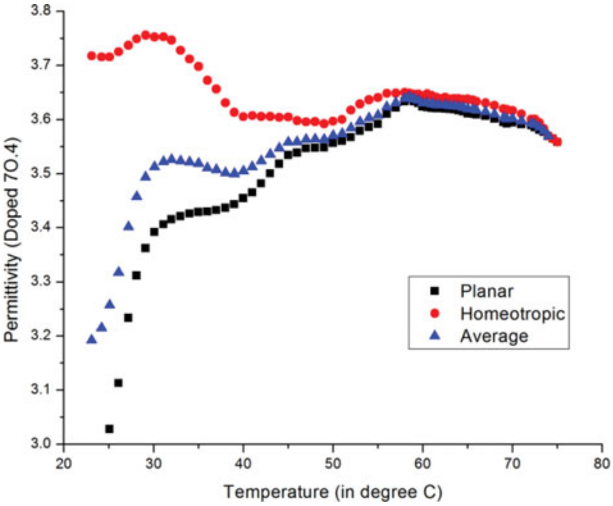

Figure 4. Static permittivity versus temperature for doped 7O.4 sample.

permittivity is higher than the extrapolated isotropic value and the permittivity values for both—parallel and planar—alignment increasing with the decrease in temperature, may also be found in other LC compounds containing alkyloxy group.

Figures 7 and 8 show the temperature dependence of the static permittivity of the pure 7O.6 and the doped 7O.6 samples, respectively. The variation of permittivity versus temperature curve for the pure 7O.6 sample (Fig. 7) is also found to be of similar form as that of the pure 7O.4 sample. The permittivity for the homeotropic alignment increases with the decrease of temperature, whereas for the planar alignment, the permittivity value increases with decrease of temperature till Sm F–Sm C transition temperature ($T = 66$ °C) and then decreases with the decrease of temperature. This could be interpreted by the changing of the parallel dipole–dipole correlation of the perpendicular dipole component to antiparallel dipole–dipole correlation for temperature below this phase transition temperature. The permittivity behavior

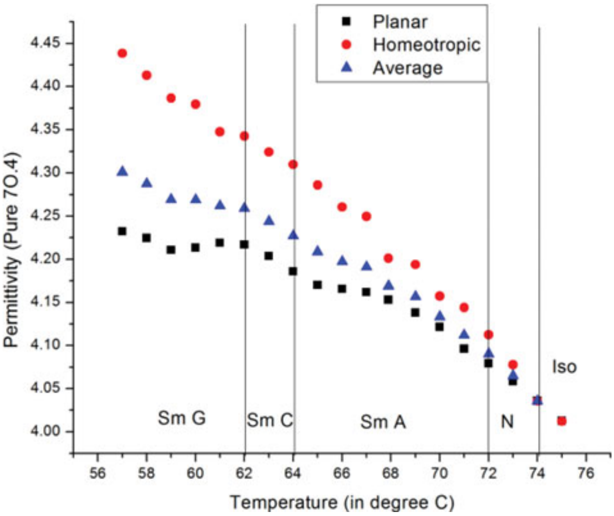

Figure 5. Temperature dependence of static permittivity of pure 7O.4 showing the phase transition temperatures.

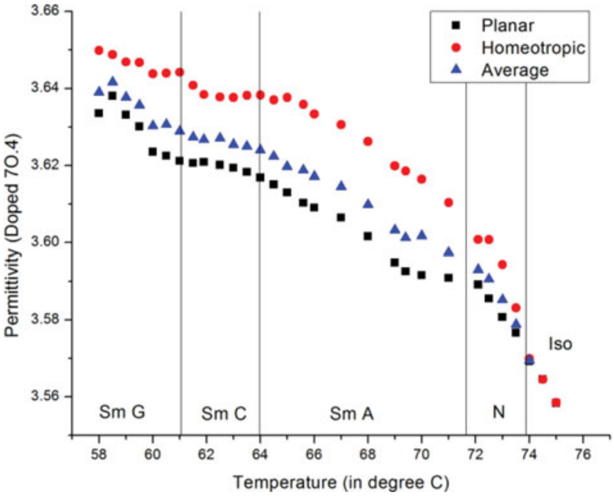

Figure 6. Temperature dependence of static permittivity of doped 7O.4 showing the phase transition temperatures.

with the variation of temperature in Sm G phase of the sample is same as that of the Sm F phase. In contrast, the parallel dipole component has only parallel dipole–dipole correlation at all temperature range studied. The behavior of permittivity in the isotropic phase of pure 7O.6 is also found to be similar to that of pure 7O.4 sample.

A comparison of our present work with that of Padmajarani et al. [9] reveals that the variation of permittivity with temperature for the homeotropic alignment is similar. That is 7O.4 and higher homologs are positive dielectric anisotropic materials. However, the lower homolog members like 6O.4 [24] and 5O.7 [25] have their permittivity values in homeotropic alignment decreasing with decrease in temperature. This implies the negative dielectric anisotropic nature of these lower homologs. Such contrasting behaviors for the lower and the higher members of the *n*O.*m* compounds suggest a change in orientation of alkyloxy dipole group w.r.t. its long molecular axis when CH_2 chain length changes. Primarily, this must be

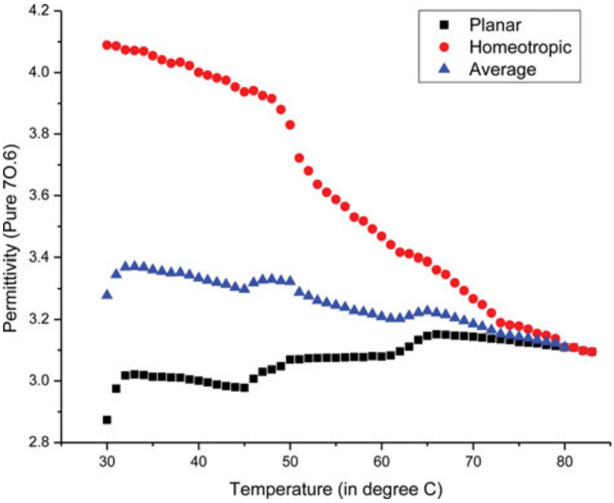

Figure 7. Static permittivity versus temperature for pure 7O.6.

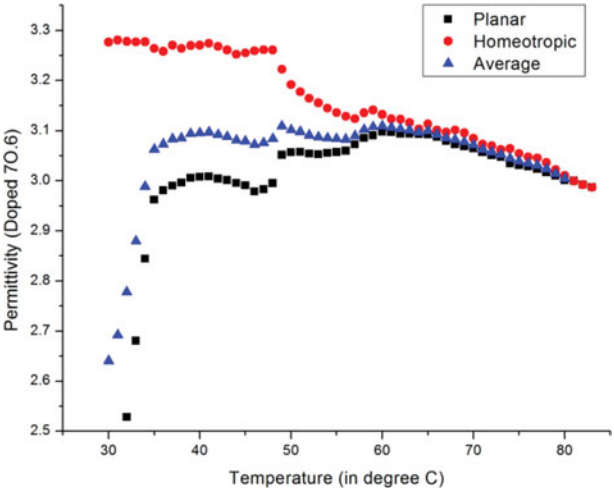

Figure 8. Temperature dependence of static permittivity for doped 7O.6.

a consequence of the strain produced on the rigid part of the molecule due to the increasing length of end chain and the modified interaction among the neighboring dipoles.

The variation of the dielectric anisotropy of the two LC samples (pure and doped)—7O.4 and 7O.6—with the variation of temperature is given in Figs. 9 and 10. In Fig. 9, one may observe that the dielectric anisotropy for pure 7O.4 sample increases with the decrease in temperature except for the anomalous behavior in Sm G phase. The gradual increase in the dielectric anisotropy may be due to a stronger degree of parallel dipole–dipole correlation for the parallel components of dipole in comparison to that for the perpendicular components (this is so because permittivity for homeotropic alignment increases relatively more than that of permittivity in planar alignment as shown in Fig. 5). The large increase and the anomalous behavior in dielectric anisotropy in the Sm G phase may be related mainly to the behavior of dipole–dipole correlation for the perpendicular component of dipole (as seen from permittivity versus temperature curve of Fig. 5 in planar alignments).

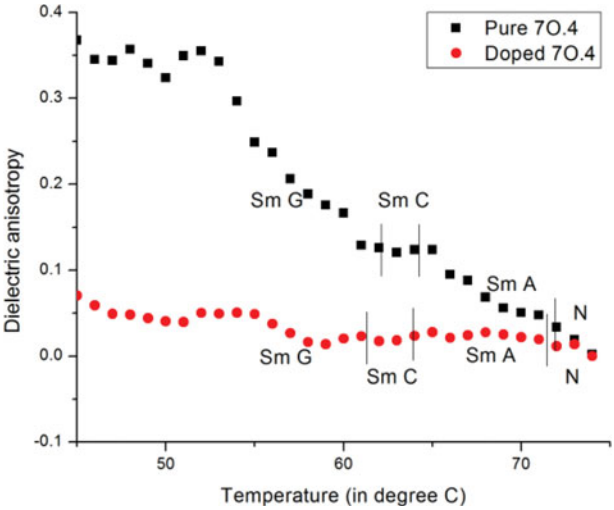

Figure 9. Dielectric anisotropy of pure 7O.4 and doped 7O.4.

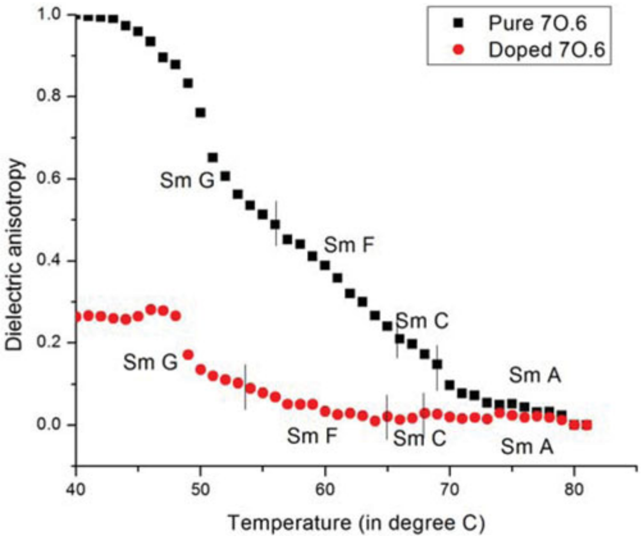

Figure 10. Dielectric anisotropy of pure 7O.6 and doped 7O.6.

In an earlier work, Bahadur et al. [26] have reported the possibility for parallel or antiparallel type of correlation between the dipoles depending on the relative distance between the dipoles in the same layer and those between dipoles in adjacent layers. So, the introduction of molecular positional ordering and the rapid reorientational motion of the molecules about their long axis in the Sm G phase [27] of our sample could possibly govern the behavior of the parallel dipole–dipole correlation between the perpendicular dipole components. It may be seen in Ref. [28] that the dipole–dipole interaction for central dipoles between the neighboring molecules in same layer is large in comparison to that between dipoles in different smectic layers.

In Fig. 10, one may observe that the dielectric anisotropy of the pure 7O.6 increases with the decrease in temperature. A comparison of the variation of dielectric anisotropy with temperature for pure 7O.6 (Fig. 10) and pure 7O.4 (Fig. 9) shows some aspects of similarity as well as differences. Though the anisotropy increases with the decrease in temperature for the samples, one finds that the anisotropy for 7O.6 is comparatively larger than that of 7O.4 sample. The slope in the anisotropy versus temperature curve is almost similar in all the smectic phases of 7O.6 except the Sm G phase. However, the slope is different in the smectic phases of 7O.4 sample. This could be due to the difference of end chain alkyl aniline of the two compounds. Both the two compounds show anomalous variations in the temperature dependence of anisotropy in Sm G phase.

3.2. *Doped 7O.4 and Doped 7O.6*

When the sample 7O.4 is doped with SNPs, the resultant permittivity versus temperature curve (Fig. 4) for the homeotropic alignment increases with the decrease of temperature while it decreases with the decrease of temperature for the planar alignment. This behavior is similar to that for the pure samples (Fig. 3). A better comparison may be made for the pure and the doped samples by studying the temperature dependence curve of dielectric anisotropy (Fig. 9). There occurs a decrease in anisotropy for the doped 7O.4 as compared to that for the pure 7O.4 sample. The variation of dielectric anisotropy with temperature for the doped 7O.4 sample is similar to that for the pure 7O.4 but with a lesser slope. Likewise, the behavior of permittivity versus temperature curve (Fig. 8) and the variation of dielectric anisotropy versus temperature curve (Fig. 10) for the doped 7O.6 sample is also similar to that for the pure 7O.6 (Figs. 7 and 10). In both the doped samples, slope is near zero for Sm C and other phases at higher temperature. A qualitative reasoning is given as follows. Since the permittivity values for the doped sample (7O.4 or 7O.6) is smaller than that of the pure sample, the (average) effective dipole moment of the doped sample must have been reduced by the doping of SNPs. This is possible if the nearest dipoles surrounding the SNPs rearrange their relative orientation resulting in such a way that a net reduction of the dipole moment takes place while dipoles far away in the bulk sample remain more or less unaffected. In other words, some disorder is introduced due to the presence of SNPs. This could also result in a reduced dielectric anisotropy. As dielectric anisotropy is an average quantity, the uniform dispersion of the nanoparticles and the redistribution (or rearrangement) of only a few LC molecules around the SNPs without affecting the far away molecules result in the similar dielectric anisotropy behavior (Figs. 9 and 10) of the doped samples to that of the pure samples. In our limited experimental condition, we cannot separate the individual effect of the capping layer or the nanoparticles as we have used only one kind of thiol capped SNPs in a certain range of size. It appears that the type of capping agent or the kind and size of nanoparticles affects the dielectric anisotropy. For example, a similar report [29] on the decrease of dielectric anisotropy may be found when the LC 4,40-di hexyl azoxy benzene (D6AOB) was doped with zinc oxide nanoparticles. But Ouskova et al. [30] reported the increase in dielectric anisotropy of nematic LC host, ZLI-4801-000 (Merk) when ferroelectric thiohypodiphosphate nanoparticles are doped. In another work, Hao Qi et al. [31] have reported that the dielectric anisotropy of pure LCs [Felix-2900-03 (Hoechst)] doped with different size of gold (or silver) nanoparticles with different capping layer decreased or increased depending on the size of the nanoparticles.

The frequency dependence of dielectric anisotropy for the pure 7O.4 (and 7O.6) and the doped 7O.4 (and dope 7O.6) samples at representative temperatures 50 °C and 67 °C are shown in Fig. 11 (and Fig. 12). It is found that the dielectric anisotropy is very small and almost a constant when the frequency is increased. However the anisotropy increases with the increase in frequency for the Sm G phase (curve corresponding to 50 °C). A similar report on

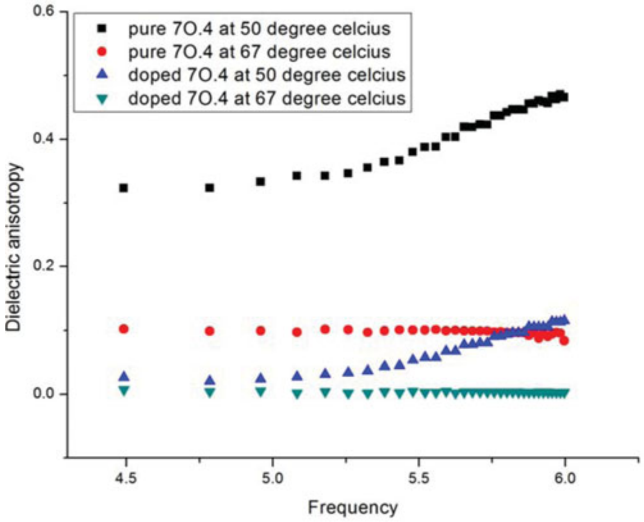

Figure 11. Frequency dependence of dielectric anisotropy for pure and doped 7O.4 samples at representative temperatures 50 °C and 67 °C.

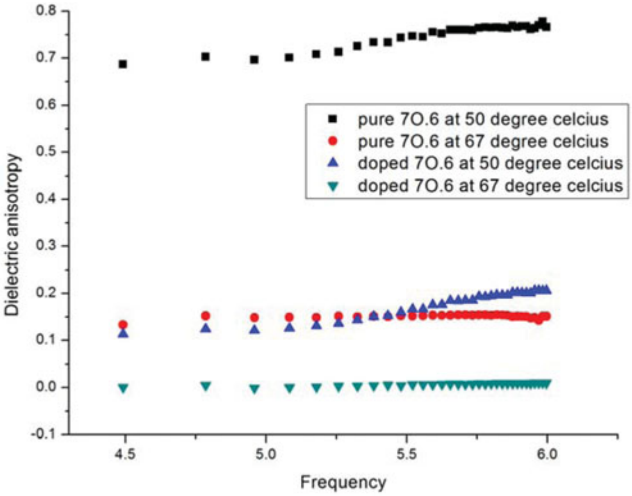

Figure 12. Frequency dependence of dielectric anisotropy for pure and doped 7O.6 samples at representative temperatures 50 °C and 67 °C.

the increasing nature of dielectric anisotropy with frequency may also be found in other LC [32]. In our present study, the slight increase in anisotropy with frequency may be due to the anomalous behavior of Sm G phase as mentioned above.

4. Conclusions

Dielectric studies of the compounds, 7O.4 and 7O.6 at low frequency indicate the existence of parallel dipole–dipole correlation in the isotropic and liquid crystalline phases. The existence of parallel dipole–dipole correlation in both the parallel and perpendicular components of dipole could be the main reason for low values of dielectric anisotropy. The degree of dipole–dipole correlation changes with the temperature. This may be responsible for the anomalous behavior of the variation of dielectric anisotropy with temperature. The resulting composite, when doped with SNPs, shows liquid crystalline properties but their dielectric anisotropy in drastically reduced due to lowering of effective dipole moment. A possible mechanism is the redistribution of orientation of dipoles near the SNPs leading to a decrease in effective dipole moment, while the orientations of the far away dipoles in the bulk remain unaffected. Consequently, the nature of the permittivity and the anisotropy versus temperature curve is similar to that of the pure sample. The study suggests that the additional dielectric properties due to the dipoles may be manipulated without affecting the liquid crystalline properties.

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