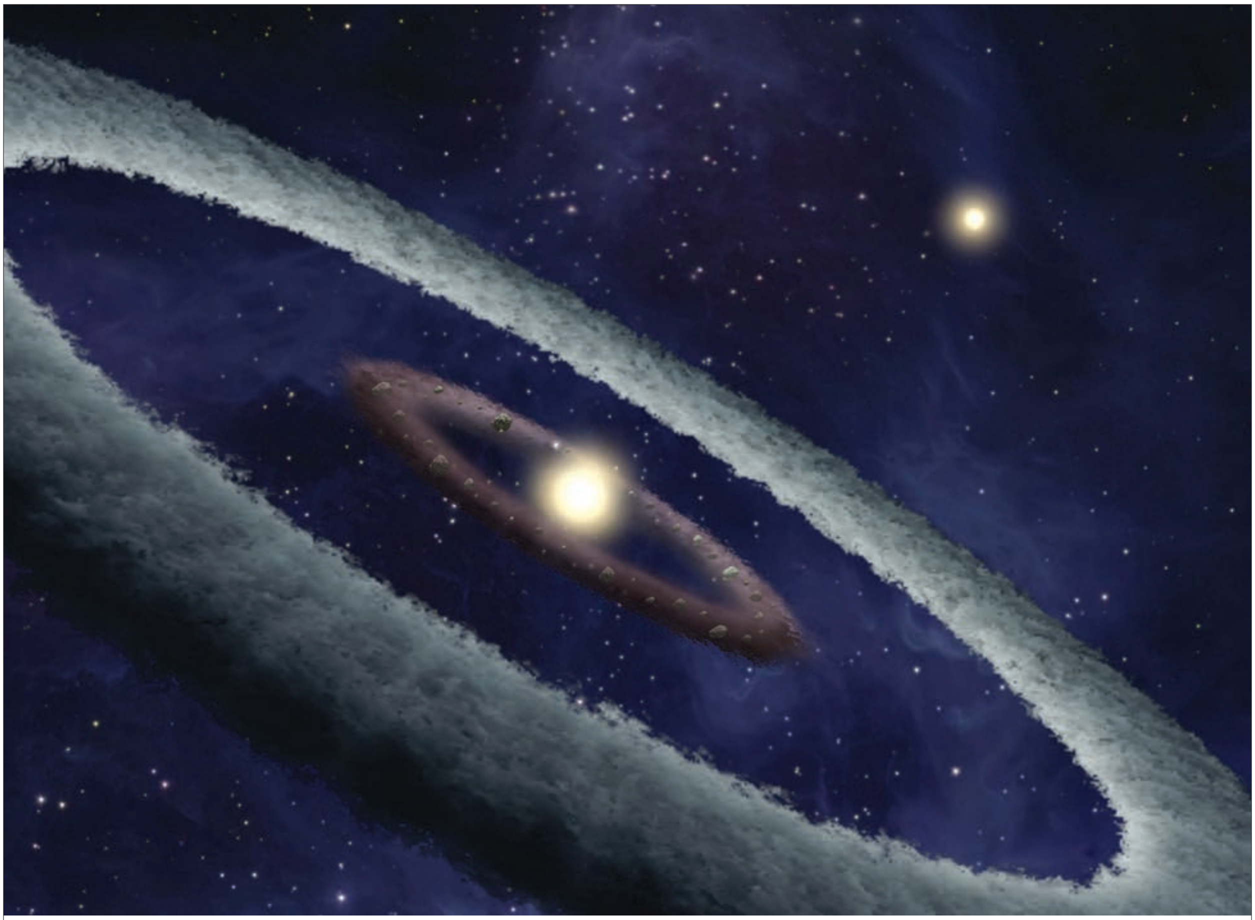

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Effect of Dichroic Dye on Dielectric and Optical Properties of a Nematic Liquid Crystal*

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Abstract: Temperature variation of dielectric loss, dielectric permittivity, dielectric anisotropy and percentage optical transmittance of nematic liquid crystalline sample B08 and its composite with dye have been reported in the temperature range of 30 to 164°C. The dielectric loss and dielectric permittivity have also been measured with variation of frequency. The dielectric studies have been conducted in the frequency range of 1 kHz to 5 MHZ. The thermodynamical parameters have also been calculated by using the dielectric loss data in the frequency range mentioned above. A comparison of dielectric and optical parameters including transition temperature of pure nematic sample with dye mixed liquid crystal indicates that a significant change take place in these properties due to addition of dye in host liquid crystal.

Key words: Doping effects, permittivity, optical properties, phase transitions

INTRODUCTION

Interest in dye mixed liquid crystals and their practical application has increased recently for a number of reasons in the field of liquid crystalline material. Fast response time and high degree of ordering in dye mixed liquid crystals has been one of the reasons for their importance in practical application. In guest host displays the liquid crystalline material used are the solution of dye (guest) in pure liquid crystals (host). The presence of dye changes various properties of liquid crystals up to a great extent. When dye is dissolved in a nematic liquid crystals, molecules of dye possessing anisotropy tend to arrange in such a way that their long molecular axis align along the liquid crystals director. It is also well known that the presence of dye in nematic liquid crystals changes the range of nematic phase, which is caused due to either increase or decrease in nematic- isotropic transition temperature (Bauman and Haase, 1989). The properties, which can be varied with the help of doping dye in liquid crystals are dielectric permittivity, dielectric loss, optical transmittance, order parameter etc. A review of literature reveals that the effect of doping dichroic dyes in liquid crystals have been investigated by some groups for their use in electro optic display devices (Raina *et al*., 1999).

Dielectric and optical studies of liquid crystals and their mixture with mesogenic and non mesogenic compounds are important as they provide valuable information on molecular arrangement, molecular motion and intermolecular interaction especially in nematic and isotropic phase (Chen and Hwang, 2004). Therefore these properties of pure nematic liquid crystals have been studied by various groups (Scarmujja *et al*., 2001). But the dielectric measurement of dye doped nematic liquid crystals are less studied as most of the studies are concentrated around electro optic effect of the dye doped liquid crystals (Shussarenko and Francescangeli, 1997; White and Taylor, 1974). Therefore it has been considered important to make systematic and detailed study of nematic liquid crystal B08 and its mixture with Anthraquinone dye in low concentration. These investigations are expected to give information regarding interaction of dye molecule with nematic liquid crystal and their contribution to the occurrence of relaxation modes.

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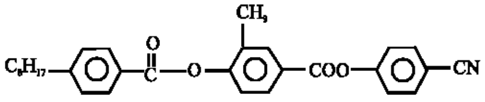
The phase transition temperature obtained using dielectric measurement technique has been supported by data obtained from optical transmittance study for pure as well as dye mixed liquid crystals.

MATERIALS AND METHODS

Material

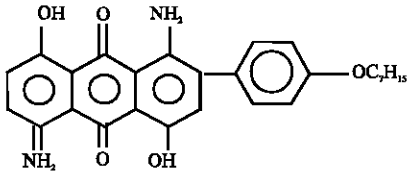
The material under investigation is a pure nematic liquid crystal B08 crystal with the following structure



Chemical structure of B08

The other sample has been prepared by mixing Anthraquinone dye in pure nematic liquid crystal in concentration 2% wt/wt. The strong interaction between two different types of molecules allows the sample to maintain a good alignment (Gibbons *et al*., 1991) which has been confirmed by observing the sample holder under polarizing microscope.

The guest host sample and pure sample has been filled in a standard sandwich type sample holder having coating of Indium Tin Oxide (ITO) on the glass substrate and pretreated with polymide for planner type alignment. The molecular structures for anthraquinone dye are given below.



Chemical structure of anthraquinone dye

Dielectric Studies

Two planar aligued and ITO coated cells of thickness 5 μ were used for the dielectric measurements. One cell is filled with pure liquid crystal and other is filled with dye doped liquid crystal. We have used an impedance/ Gain phase analyzer (HP-4194A) to determine the real and imaginary part of permittivity. The values of Cp and Dp have been read on the screen of analyzer first without sample and then after introducing the sample in the cell. These measurements have been taken in the frequency range of 1 kHz to 5 MHZ for different temperatures. In order to vary the temperature a microprocessor based heating device Julabo-F 24 has been used. The real and imaginary part of permittivity have been determined by using the values of capacitance and dissipation of empty sample holder and sample holder filled with sample as described in our earlier work (Singh *et al*., 2005) by following equation (Manohar *et al*., 2006).

$$\varepsilon' = \frac{C_m - C_O}{C_1} + 1 \qquad (1)$$

It directly gives the value of perpendicular component of dielectric permittivity $\varepsilon_\perp$ as we are using planer aligued sample holders. The values of $\varepsilon_\perp$ after the N→I transition temperature become equal to ε_i (dielectric permittivity in isotropic phase) and varies almost linearly with temperature in isotropic phase. By extrapolating this for nematic phase we can obtain the value of ε_{avg} or $\bar{\varepsilon}$ for the sample. Now ε_{II} can be calculated using the following relation (Bahadur, 1991)

$$\bar{\varepsilon} = \frac{\varepsilon_{11} + 2\varepsilon_{\perp}}{3} \qquad (2)$$

Thermodynamical parameters have been determined by using the dielectric relaxation data with following equations

$$\text{Relaxation time } \tau = 1/\omega \qquad (3)$$

Where $\omega = 2\tau f$ where f is the frequency of the applied electric field.
Thermo dynamical parameter ΔF, ΔH and ΔS are related by the following equation

$$\tau = h/kT\ (\exp F/RT) \qquad (4)$$

$$\text{Where } \Delta F = \Delta\ H - T\Delta\ S \qquad (5)$$

Optical Studies

For optical transmittance measurements sample holder filled with sample is placed on rotating stage between two crossed polarizers of polarizing microscope, model CENSICO (7626). A detector has been fitted at one of the eyepieces of microscope to monitor the change in intensity of light transmitted. The temperature of the sample has been varied by using a refrigerated circulator of Julabo (Model No. F-25) with accuracy of ±0.1° C. The variation of temperature gives rise to change in phase of the sample. This allows the light of different intensity to transmit through the sample and incident on detector. The optical transmittance data has been normalized by considering 100% transmittance through empty cell and 0% transmittance through sample holder filled with black ink.

RESULTS AND DISCUSSION

Figure 1 and 2 represent typical frequency dependences spectra of the real and imaginary part of the dielectric permittivity measured for pure liquid crystal and dye doped liquid crystal. The real part of dielectric permittivity is either constant or decreases as the frequency has been increased (Viciosa *et al*., 2002). Low values of ε' at higher frequency suggest that the molecule rotate about their molecular axis (Arora and Agarwal, 1991) or some of its side group rotates and give rise to this kind of relaxation. This type of low frequency relaxation has also been reported by other workers for nematic liquid crystals (Biradar *et al*., 2000). The variation of dielectric permittivity with frequency shows almost similar behaviour for pure liquid crystal and dye doped liquid crystal but the values of permittivity are higher for dye mixed liquid crystal.

Maxima in loss curve has been observed at frequency 125 kHz for pure liquid crystal and observed at frequency 400 kHz for dye doped liquid crystal. The peak in the curve indicates dielectric relaxation and it shift towards higher frequency side as expected and also reported by other investigators (Bahadur, 1990). Each curve in Fig. 4 shows similar behaviour on both side of the peak and this type of behaviour has also been observed by many other researchers for nematic, smectic and cholesteryl liquid crystals (Thakur *et al*., 2003).

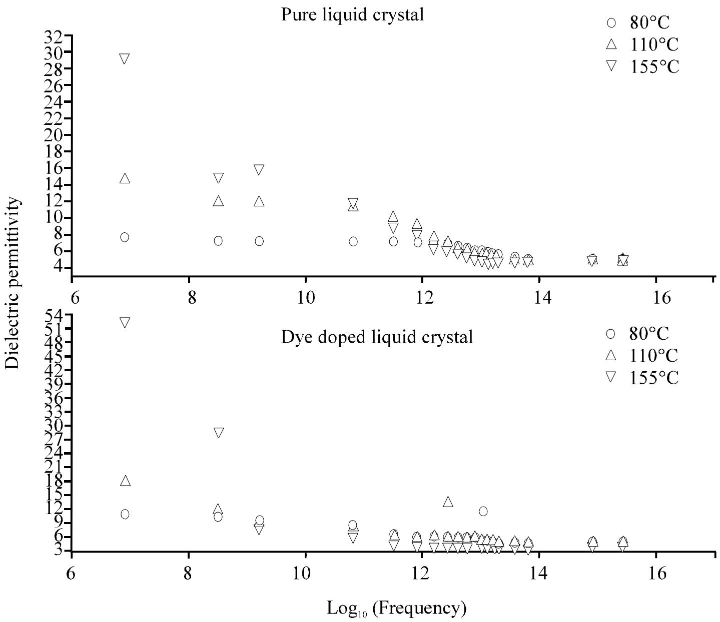


Fig. 1: Variation of dielectric permittivity with log of frequency for pure liquid crystal and dye doped liquid crystal

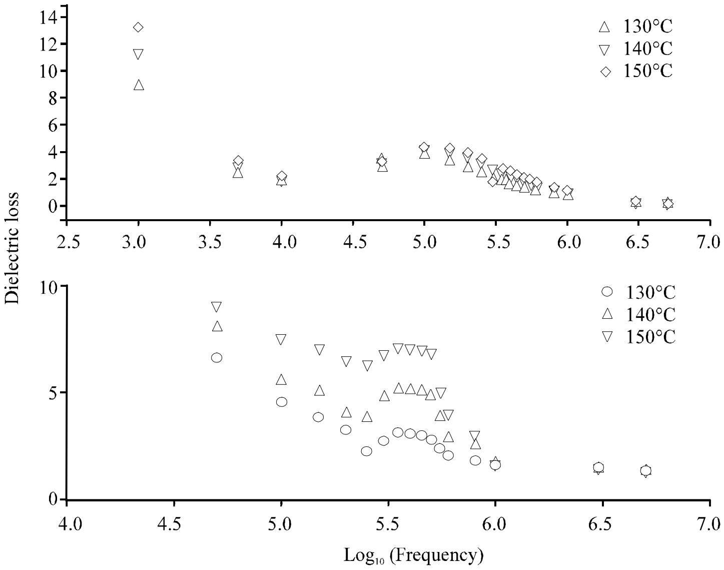


Fig. 2: Variation of dielectric loss with log of frequency for pure liquid crystal and dye doped liquid crystal

The nature of loss curve is similar for pure liquid crystal and dye doped liquid crystal but it is evident from the Fig. 3 that the peak of the curve obtained for pure liquid crystal has been significantly shifted from the frequency of the peak obtained for dye doped liquid crystal. It suggests that the

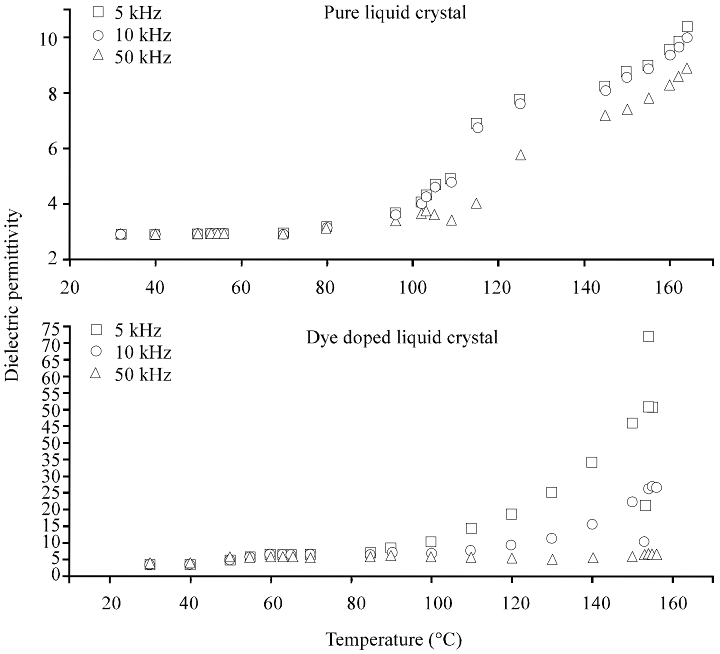


Fig. 3: Variation of dielectric permittivity with temperature for pure liquid crystal and dye doped liquid crystal

relaxation frequency of the dye-doped liquid crystal is different from that of pure sample and the variation also depends upon the type of dye used and the compatibility of dye with liquid crystal host.

The variation in the value of ε′ and ε′′ due to addition of dye can be explained by considering the contribution of dipole moment of dye molecule in the host liquid crystal molecule. Each dye molecule has a preferential axis of orientation, which will get aligned along with the host liquid crystal molecule therefore resulting in the restriction on the freedom of movement. Thus the dipole moment of dye molecule contributes significantly to the actual value of ε′ and ε′′ and also to the relaxation frequency value (Hohmutha and Schieweb, 1981).

Figure 3 and 4 shows the variation of ε′ and ε′′ as a function of temperature for pure liquid crystal and dye doped liquid crystal. The values of real part of permittivity remain almost constant in temperature range of 30 to 100°C and its value varies slightly at 103°C shows crystalline to nematic transition of sample and a sharp change in its value at 163°C shows that sample become isotropic at this temperature. This type of behaviour has also been reported by other groups for other type of liquid crystal sample (Agrawal *et al.*, 1989). Similar type of behaviour has also been observed for the curve of ε′′ versus temperature at varying frequencies shown in Fig. 5.

The transition scheme determine by dielectric study is as follows

$$\text{Mix 1 Crystt.} \xrightarrow{102^\circ\text{C}} \text{Nematic} \xrightarrow{163^\circ\text{C}} \text{Isotropic}$$

$$\text{Mix 2 Crystt.} \xrightarrow{100^\circ\text{C}} \text{Nematic} \xrightarrow{156^\circ\text{C}} \text{Isotropic}$$

The small difference in the experimental value from literature values of transition temperature can be attributed to the influence of boundary condition on phase transition temperature for sample.

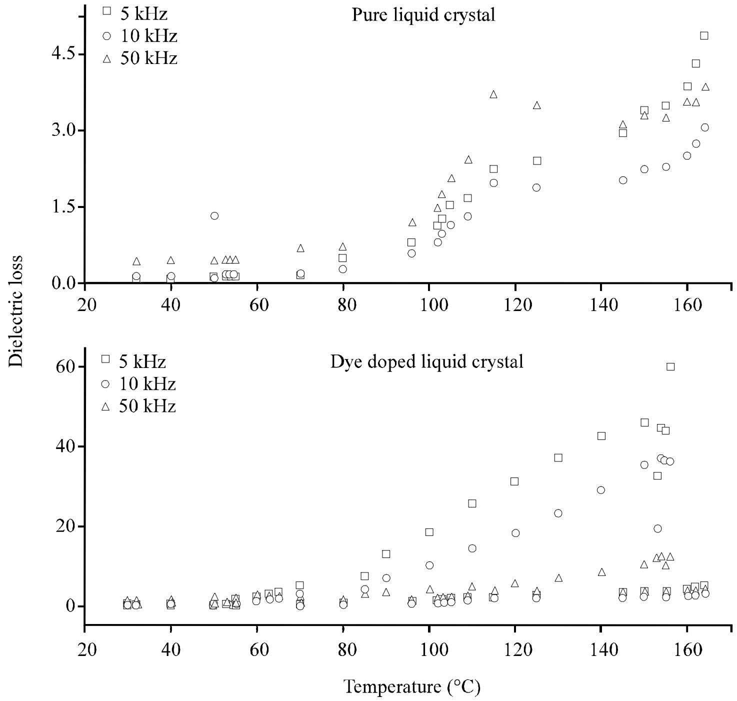


Fig. 4: Variation of dielectric loss with temperature for pure liquid crystal and dye doped liquid crystal

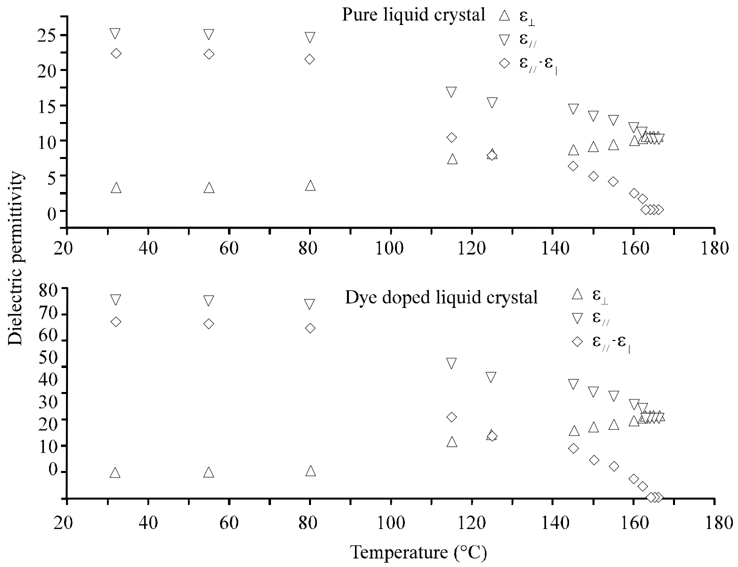


Fig. 5: Variation of ε_{11} and ε with temperature for pure liquid crystal and dye doped liquid crystal

Enthalpy of activation energies was found to 1.11 kcal mol^{-1} deg for pure liquid crystal and 1.25 kcal mol^{-1} deg^{-1} for dye doped liquid crystal. For guest host sample energies are slightly higher than the pure liquid crystal which implies an increase in the hindering potential barrier in guest host

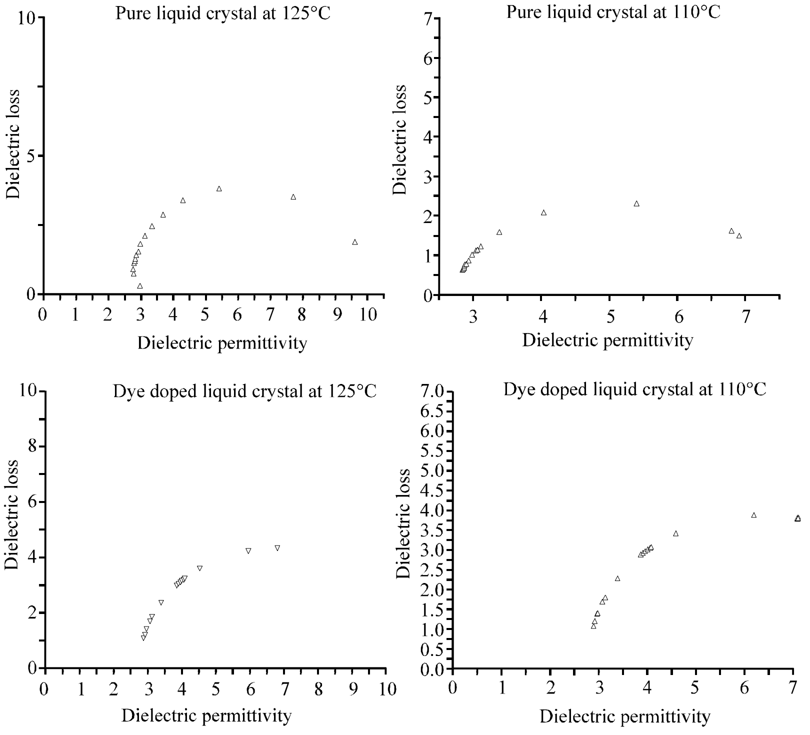


Fig. 6: Cole-Cole plot for pure liquid crystal and dye doped liquid crystal at 110 and 125°C

sample. In other words guest host sample requires a higher energy to overcome the hindering potential barrier and to realize a rotational motion (Haase and Wrobel, 2003; Agrawal *et al*., 1989).

Dielectric anisotropy has been calculated from the data of dielectric permittivity corresponding to the various applied frequencies. The variation of ε_{11} and $\varepsilon_{\perp}$ with temperature are shown in Fig. 5. Pure liquid crystal and dye doped liquid crystal shows almost similar behaviour. For Pure liquid crystal the values of $\varepsilon_{\perp}$ remains constant in crystalline phase and then increases slowly up to a temperature until sample becomes isotropic. After that the values remain constant with further increase of temperature but the values of ε_{11} remains constant in crystalline phase and then decreases slowly up to the point sample becomes isotropic and after this the values remain constant. Similar type of behaviour has been observed in the case of dye doped liquid crystal.

The present data can also be represented by the symmetrical distribution, which has been indicated by Cole-Cole plot. Representative curve at 110, 125°C for pure liquid crystal and dye doped liquid crystal are shown in Fig. 6. For the qualitative analysis of the dielectric spectra the Cole -Cole equation has been used

$\varepsilon^*(\omega) = \varepsilon'(\omega)-i\varepsilon''(\omega)$

$$= \varepsilon_{\infty} + \sum \frac{\Delta\varepsilon}{1+(i\omega\tau)^{1-\alpha}} \qquad (6)$$

Here ε_{∞} is the high frequency limit of the permittivity; $\Delta\varepsilon$ is dielectric strength and τ is mean relaxation time. The exponent ∝ (0<∝<1) represent the distribution of relaxation times and goes to zero when single relaxation is effective. Both the real and imaginary part of permittivity has been analyzed.

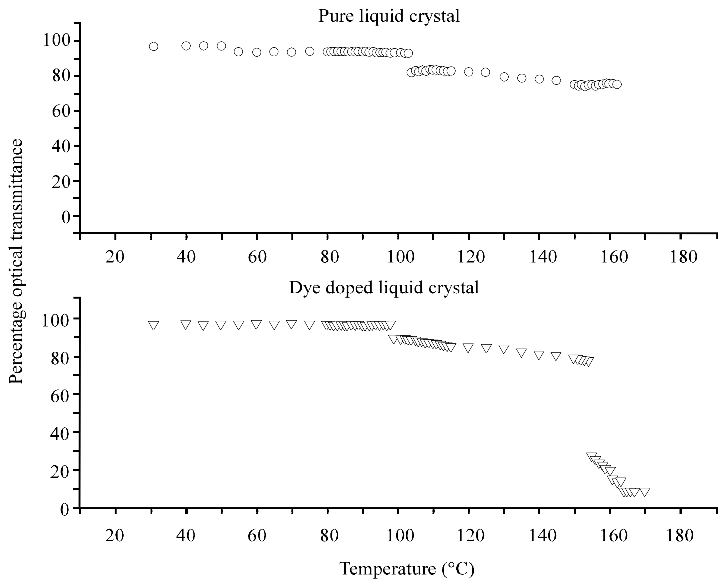


Fig. 7: Variation of percentage optical transmittance with temperature for pure liquid crystal and dye doped liquid crystal

The fitting of the Cole-Cole equation to the experimental spectrum has been performed and it has been found that the centre of Cole-Cole plot lies below the real axis indicating distribution of relaxation time (Manohar *et al*., 2000).

The optical transmittance data as a function of temperature has been plotted for pure liquid crystal and dye doped liquid crystal. Figure 7 shows the variation of percentage optical transmittance with temperature.

The samples show following phase sequence as determined by optical transmittance measurement

Pure liquid crystal	Crystt. $\xrightarrow{104°C}$ Nematic $\xrightarrow{163°C}$ Isotropic
Dye doped liquid crystal	Crystt. $\xrightarrow{99°C}$ Nematic $\xrightarrow{155°C}$ Isotropic

The phase transition temperature measured for the dye doped liquid crystal is not same as in case of pure liquid crystal. It can be concluded that, when dye has been mixed in pure nematic sample the value of transition temperature decreases in comparison to pure sample. But the breath of nematic isotropic phase has been found to increase slightly in comparison to pure sample. This type of behaviour has also been reported by our group (Demus *et al*., 1978) and other workers (Shussarenko and Francescangeli, 1997) for cholesteric as well as nematic samples. Singh *et al.* (1990) have also observed similar behaviour and concluded that the breadth of the transition depends upon the purity of substance and it decreases with lower of purity.

CONCLUSIONS

- The measurement of dielectric parameters, optical transmittance and dielectric anisotropy show the Iso-Nem and Nem-Cryst phase transitions.
- Transition temperature obtained from different techniques i.e., optical transmittance, dielectric and birefringence measurements are found to be in good agreement.

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