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Dielectric and optical study of 4-n-decyloxybenzylidene 4'-iso propylaniline exhibiting monotropic smectic a phase

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ABSTRACT

The dielectric measurements have been done for the determination of real and imaginary part of permittivity of a newly synthesized monotropic smectic sample. The sample has been investigated in the frequency range from 1kHz to 1MHz and temperature range 315K to 340K. The dielectric measurements in smectic phase indicate Debye-type dispersion with relaxation peak at 357.72kHz for 333 K and activation energy was found to be 2.44KJmol^{-1}. Measurements have also been made for refractive indices, birefringence, optical transmittance in the above mentioned temperature range and order parameter have been calculated using birefringence data .The temperature dependence of these parameters have been discussed in detail. The phase transition temperature matches very well as obtained from the study of dielectric parameters, refractive indices and optical transmittance.

INTRODUCTION

The dielectric studies provide useful information about molecular structure, molecular dynamics, phase transition and display performance of liquid crystals[1-5]. Most of the dielectric studies on liquid crystals are concentrated in nematic phase and nematic- isotropic phase transition[4]. Dielectric studies on smectic phase are very scanty[4]. The optical characteristics, threshold voltage, switching time etc. are also strongly dependent on absolute value of dielectric constant[6]. Dielectric relaxation studies provide one of the few techniques for finding the nature of molecular reorientation and there have been several studies on liquid crystals[7-11].

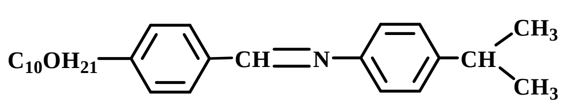
The knowledge of optical anisotropy and refractive indices of liquid crystals and their temperature dependence is of much importance from application point of view[12,13]. Order parameter is one of the important parameter of liquid crystal, which governs nearly all its physical properties[14,15]. According to de Gennes any of the bulk tensorial properties like elastic constants, electric and magnetic succeptibilities and refractive indices can be used to determine macroscopic order parameter[14,16]. This macroscopic order parameter (Q) calculated by different parameters can differs among them and also differs or be same from microscopic order parameter introduced by Tesvetaov given by $S= 1/2< 3 \cos^2\theta - 1>$[17,18] where S is order parameter and θ is the angle between director and long molecular axis of the molecule. Several methods for the determination of order parameter have been developed due to its great importance. Among those methods optical methods are most commonly used because data obtained by optical measurements are most accurate and precise. Optical transmittance study is one of the most popular techniques to investigate the phase transition temperatures of liquid crystal due to its accuracy and convenience.

In the present paper results of the measurement of dielectric constant (ε') and dielectric loss (ε'') with the variation of frequency and temperature have been reported. Cole-Cole plots have been drawn to investigate relaxation. Refractive index and its anisotropy have been measured and reported whereas macroscopic order parameter has been evaluated by anisotropy data. Optical transmittance value has been measured with the variation of temperature to study the phase transition behavior.

EXPERIMENTAL

The real and imaginary part of the permittivity of the sample have been calculated by the value of capacitance and dissipation factor, which are determined with the help of impedance/gain phase analyzer of HP-4194A. The detailed process is explained in our earlier paper[11]. Refractive indices values have been measured with the help of Abbe's refractometer (MITTAL 1245) whereas optical transmittance measurements have been done on polarizing microscope(CENSICO 7626). The constant required temperature has been obtained by microprocessor based temperature controller Julabo F-25 in all studies.

The investigated sample, 4-n-decyloxybenzylidene



4'-isopropylaniline having above structural formula, was prepared from 4-n-decyloxybenzaldehyde and 4-isopropylaniline by the method described in our previous work[19].

The product, after crystallization from ethanol, was TLC pure and exhibited monotropic SmA mesophase with the phase length of 12°C. Transition temperatures: Cr (333 K) smectic A (337 K) Iso[19].

Theory

The relationship between refractive index parallel ($n_{||}$) and perpendicular ($n_{\perp}$) to the direction of molecular axis and macroscopic order parameter can be obtained by modifying the appropriate equation[19] as

$$n_{||} = \bar{n} + \frac{2}{3} Q \cdot \Delta n \quad (1)$$

$$n_{\perp} = \bar{n} - \frac{1}{3} Q \cdot \Delta n \quad (2)$$

where $\bar{n}$ is the average refractive index and Δn is the birefringence corresponding to complete alignment $n_{||} = n_e$, $n_{\perp} = n_o$[20,21]. From both (1) and (2), we get

$$Q = \frac{n_{||} - n_{\perp}}{\Delta n} = \frac{n_e - n_o}{\Delta n} = \frac{\delta n}{\Delta n} \quad (3)$$

Where $\delta n = n_e - n_0$

The value of macroscopic order parameter equal to1 represents complete order at absolute temperature that is at 0 K $\delta n = \Delta n$. So the macroscopic order parameter (Q) has been obtained by extrapolating δn for T = 0K. This extrapolation is done on the linear portion of the graph drawn between birefringence δn against ln (1- T/T_c) as evaluated by others,[19,22] here T_c is the smectic to isotropic phase transition temperature.

RESULTS

The TABLE 1 showing the values of dielectric

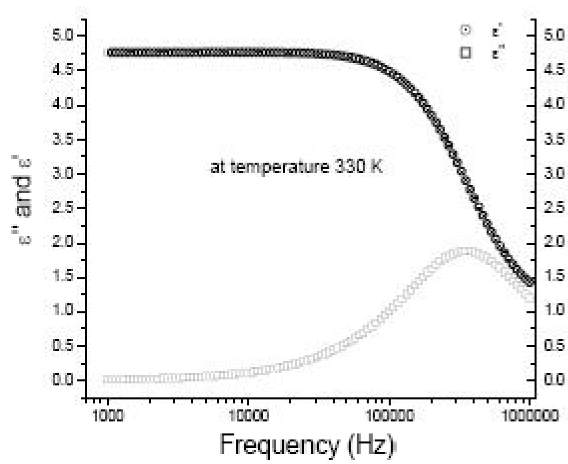


Figure 1: Frequency variation of dielectric constant and dielectric loss in SmA phase

TABLE 1: Variation of dielectric strength with temperature

Temperature (K)	Dielectric strength
333	3.77704
332	3.684917
331	3.595041
330	3.507357
329	3.421812
328	3.338353

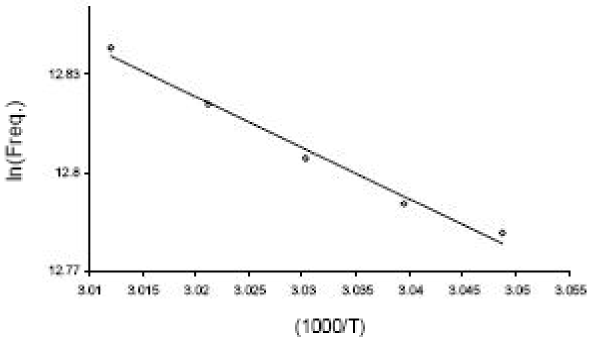


Figure 2 : Temperature dependence of relaxtion frequency

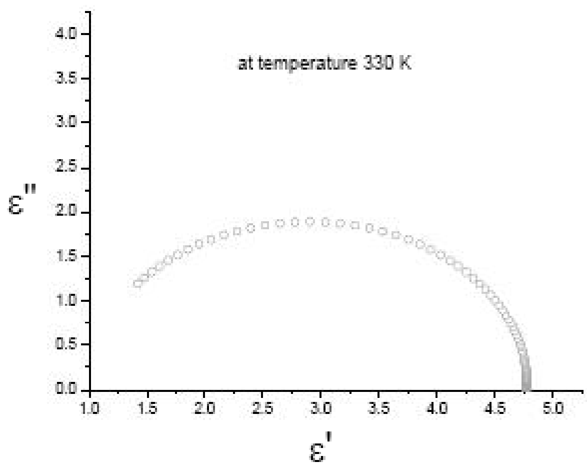


Figure 3: Cole-Cole plot of the sample at SmA phase

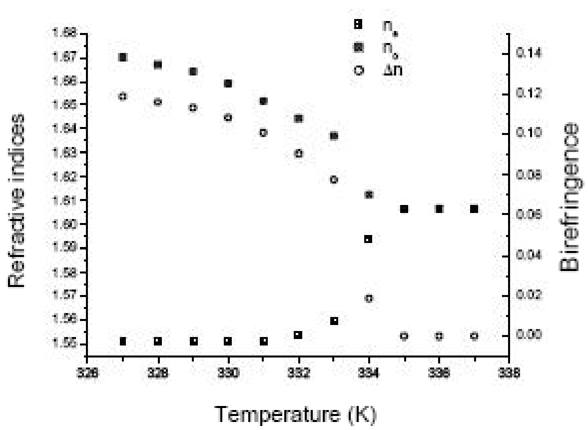


Figure 4: Plot of refractive indices and birefringence with temperature

strength with the variation of temperature has been shown. The dielectric constant (ε') and the dielectric loss (ε'') have been plotted with natural log of frequency in smectic A phase at temperature 330 K and is shown in figure 1. Figure 2 represents the relaxation frequencies of the sample as a function of reciprocal temperature in smectic A phase. The representative Cole- Cole plot of the sample at SmA phase is shown in figure 3. The plot of refractive indices and birefringence with temperature is given in figure 4. The macroscopic order parameter of the sample has been plotted with temperature and is given in figure 5. The variation of optical transmittance with temperature is shown in figure 6.

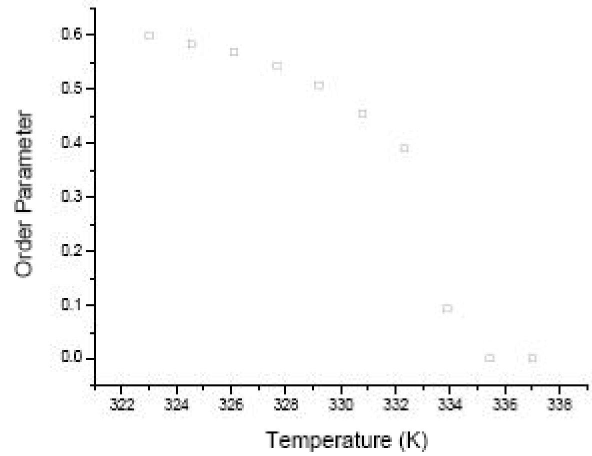


Figure 5: Order parameter versus temperature

DISCUSSION

Figure 1 show the variation of dielectric constant (ε') and dielectric loss (ε'') with natural log of frequency in smectic A phase in frequency range 1 kHz to 1MHz at temperature 330 K. The temperature dependence of dielectric constant and loss in smectic A phase is almost negligible that is why only one representative curve have been shown. The value of dielectric constant (i.e. almost 4.8) is almost unaffected for the variation of frequency upto 60 KHz and after that the value of dielectric constant decreases with increase in frequency and reaches to the value 1.5 at 1 MHz. Dielectric loss curve is also almost temperature independent. The dielectric loss for temperature 333 K initially increases with the frequency and attains a peak at 357.72KHz. Then it decreases steadily upto the measured frequency i.e. 1 MHz. The dielectric relaxation frequency peak of sample corresponds to maximum loss. The relaxation observed at high frequency is may be due to rotation of terminal group present in the molecule.

The relaxation frequency obtained frequency ob-

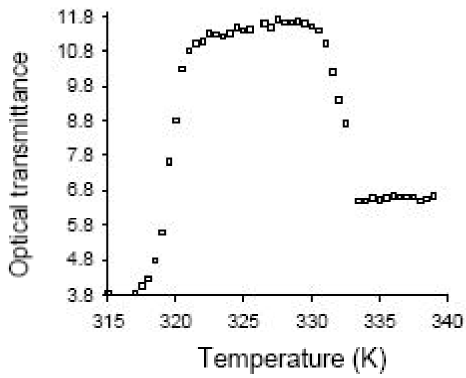


Figure 6: Optical transmittance against temperature

tained for different temperature in Sm A phase and its natural log has been plotted with $10^3/T$ in figure 2. The plot of ln(frequency) vs. $10^3/T$ yield a straight line. The activation energy calculated from the slope of this plot in smectic A phase is found to be 2.44 $KJmol^{-1}$.

The Cole-Cole plot for the sample in smectic A phase has been shown in figure 3. The points lie on semicircle with its centre on the ε' axis. The Debye's type Cole-Cole plot found here is almost temperature independent for the quantitative analysis of dielectric spectra, the Cole-Cole equation has been used[24].

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1-(i\omega\tau)^{1-\alpha}} \quad (4)$$

Here $\varepsilon\infty$ is the high frequency limit of the permittivity, $\varepsilon_o - \varepsilon_\infty$ is dielectric strength, τ is the mean relaxation time and α represents the distribution of relaxation time. The calculated dielectric strength values are given in TABLE 1.

The temperature variation of refraction indices & optical birefringence has been plotted in figure 4 in temperature range 338K to 326K. The value of ordinary refractive index is almost constant where as the extraordinary refractive index decreases. Then the value of ordinary as well as extraordinary refractive index approaches sharply to isotropic refractive index & becomes same at smectic A - Iso transition temperature after that the refractive index decreases almost linearly with the temperature like any liquid. The optical birefringence value which is 0.1189 at 327K decreases slowly with increase in temperature upto 330K with value 0.1021.Then its value decreases sharply with increase in temperature and becomes zero at smectic A - Iso transition temperature.

The macroscopic order parameter calculated by the value of optical birefringence data with the variation of temperature is presented in figure 5. The value of order parameter indicates the degree of orderness of the molecule. Therefore the decrease in value of order parameter from 0.5993 at 323K to 0.4884 at 330K indicates the increase in randomness of the molecule finally at smectic A - Iso transition temperature the order parameter value reaches to zero shows highest degree of randomness i.e. isotropic behaviour of the sample.

Figure 6 shows the variation of optical transmittance. The values of optical transmittance presented in this graph are taken in arbitrary unit .The lower optical transmittance value be almost constant in isotropic phase till 333K. Then its value increases abruptly by lowering the temperature indicates isotropic - smectic A phase transition temperature. The higher value of optical transmittance is almost unaffected with decrease in temperature upto 321^0K and after that its value decreases sharply again indicating smectic A - Cr phase transition temperature.

CONCLUSION

The various conclusions can be drawn from the results obtained by the experimental investigations

The transition temperatures obtained by optical transmittance technique is well matched with the value obtained by polarizing microscope as well as reported value[19].

The refractive index values have been measured and so the optical birefringence and macroscopic order parameter have been calculated.

The dispersion in the value of dielectric constant and dielectric loss has been found and single relaxation is obtained and Cole -Cole plot is drawn.

The temperature dependence of the relaxation frequency gives the value of activation energy.

The variation of dielectric constant and dielectric loss with temperature is not very much significant.

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