Vol. 4 (2000) Nos.1-4. **Journal of International Academy of Physical Sciences** pp.11-19

Study of Dielectric Anisotropy, Density and Optical Transmittance of Cholesteryl Propionate, Cholesteryl Benzoate and their Mixtures

Rajiv Manohar, Piyush Shukla, Isht Vibhu, Manisha Gupta
and
J. P. Shukla
Department of Physics, Lucknow University, Lucknow-226 007.

(Received November 3, 2000)

Abstract : In order to investigate the phase transition behaviour of cholesteryl propionate, cholesteryl benzoate and their mixtures with change in temperature, measurement of dielectric anisotropy (Δε) and density have been made in solid (crystalline), cholesteric and isotropic phase in the temperature range of 80°C to 180°C. Percentage optical transmittance has also been measured to examine the transitions observed by other techniques. The observed parameters clearly indicate sharp discontinuities at solid-cholesteric, cholesteric isotropic transition points suggesting first order phase transition.

Introduction

The dielectric anisotrpy (Δε) in liquid crystals resulting from the angular correlations between the moleculs not only throws light on the individual molecular structure but also on their ordering in the mesophase[1,2,3]. The knowledge of Δε and its temperature dependence are also important from the technological point of view[1,2,3]. In uniaxial liquid crystals, the dielectric permittivity is a second rank tensor; its diagonal elements are $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$, the parallel and perpendicular permittivity values, as referred to the average direction of the long axis[4].

The dielectric anisotropy (Δε) is given by

$$\Delta\varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp}$$

It is a function of molecular polarizability and depends on the magnitude and orientation of the permanent dipolar electric moment.

It is widely known that the molecular structure of liquid crystals is dependent on the

Key words : Dielectric anisotropy, Optical transmittance, Density.

temperature. There are certain ranges of temperature in which a particular molecular arrangement (or phase) exists and on heating or cooling it, the structure changes. Some structures lend themselves to practical applications, some do not; hence, it is important to know the working temperature range of any liquid crystal based device.

The usual methods of determining phase transition temperatures involve recognition of changes of appearance of the sample using hot stage optical microscopy or detection of enthalpy changes using differential scanning calorimetry(DSC), etc. Due to the nature of liquid crystal molecules the dielectric constant parallel to the long molecular axis ($\varepsilon_{\|}$) and perpendicular to it ($\varepsilon_{\perp}$) are different, giving rise to the dielectric anisotropy. It may change sign or vary discontinuously when phase transition takes place[5, 6].

There have been several studies on the dielectric anisotropy ($\Delta\varepsilon$) of nematic and smectic liquid crystals[7,8]. However, only few such studies on cholesteric liquid crystals are available in literature[4,9]. Therefore, in the present paper study of dielectric anisotropy of cholesteryl propionate, cholesteryl benzoate and their three mixtures of weight fractions 0.25 [75% cholesteryl propionate and 25% cholesteryl benzoate], 0.50 [50% Cholesteryl propionate and 50% cholesteryl benzoate] and 0.75 [25% cholesteryl propionate and 75% Cholesteryl benzoate] have been reported. The measurement of phase transition temperature and their change with the mixing is also given.

The phase transition temperatures of all the samples are further supported by the data obtained using optical transmittance measurement and density measurement techniques. The results of phase transition temperatures observed from the above three techniques have also been compared in the present paper.

2. Experimental Details

The dielectric data have been obtained using HP Impedance/gain phase analyser (No. HP 4194A) in the temperature range of 80°C to 180°C, at the frequency of 20 kHz. The dielectric permittivity (ε') for unaligned sample was determined by measuring the capacitance of the sample holder with and without sample.

For measuring $\varepsilon_{\perp}$, standard sandwich cells with transparent and conductive electrodes, purchased from Linkam Scientific Co. Ltd. England, have been used. For calibrating the cell, it is filled with pure grade standard liquids like toluence and cyclohexane. The capacitance of the cell filled with liquid and empty cell, having air as dielectric are measured at same temperature and frequency. These two data sets yield the live capacitance (CL) of the cell,

$$C_L = \frac{[\,C(st) - C_a\,]}{\varepsilon'(st) - 1} \tag{1}$$

where C_a is the capacitance of empty cell, $C(st)$ is the capacitance of the cell filled with standard liquid and $\varepsilon'(st)$ is the dielectric constant of standard liquid.

After calibrating the cell it was filled with the sample by capillary action. For this purpose, the samples are filled at about 10°C above the transition temperature to isotropic phase. The dielectric constant in perpendicular direction ($\varepsilon\perp$), has been determined using the following equation

$$\varepsilon_{\perp} = \frac{C_m - C_a}{C_L} \qquad (2)$$

where C_m is the capacitance of the cell with sample, C_a is the capacitance with air and C_L is the live capacitance of the sample holder. Dielectric anisotropy has been determined by measuring $\varepsilon\perp$ and ε of the aligned and unaligned samples and calculating $\varepsilon_{\parallel}$ with the help of isotropic averages[10].

For measuring percentage optical transmittance, a capillary tube of 1 mm diameter was filled with sample in isotropic phase. After removing air bubbles from it, the tube is sealed and cooled down. The optical transmittance was measured in the temperature range of 80°C to 180°C.

The density was measured using a precise dialatometer and traveling microscope of least count 0.001 cm in the above mentioned temperature range.

3. Results

The variation of dielectric constant in parallel ($\varepsilon_{\parallel}$) and perpendicular ($\varepsilon_{\perp}$) direction and dielectric anisotropy ($\Delta\varepsilon$), with temperature for pure samples are shown in Fig. 1. Variations of these parameters for mixtures are shown in Fig. 2. The plot of optical transmittance versus temperature for different samples is given in Fig. 3. The graphical presentation of density (ρ) versus temperature is given in Fig. 4. The values of transition temperatures are given in Table 1 for all the samples. The variation of the S-Ch and the Ch-I transition temperature with concentration of cholesteryl benzoate have been shown in Fig. 5 and 6, respectively.

4. Discussion

4.1 Dielectric Anisotropy Measurement

The dielectric anisotropy ($\Delta\varepsilon$) and components of dielectric constants $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$, for pure samples are shown in Fig. 1 with increasing temperature. For both the samples $\varepsilon_{\parallel}$ decreases and $\varepsilon_{\perp}$ increases and hence $\Delta\varepsilon$ decreases with the increasing temperature. The samples, i.e., cholesteryl propionate and cholesteryl benzoate go into isotropic phase at 95°C and 175°C, respectively, as is evident from the disappearance of dielectric anisotropy at these temperatures.

Further, dielectric anisotropy is higher in solid phase than in cholesteric phase indicating increased order in solid phase. For cholesteryl propionate the dielectric anisotropy shows a sharp decrease at 90.5°C as the sample goes into cholesteric phase. Cholesteryl benzoate shows such a change for the S-Ch transition at 149°C. It is seen that the temperature dependence of $\Delta\varepsilon$ is nearly linear with a slight deviation at transition points $\varepsilon_{\perp}$ has been found to vary more rapidly with temperature, exhibiting both the phase transitions more distinctly. The transitions are easily observed by the discontinuities in these curves, which suggest that they are of the first order. The nature of such transitions could be ascertained by specific heat measurements[11].

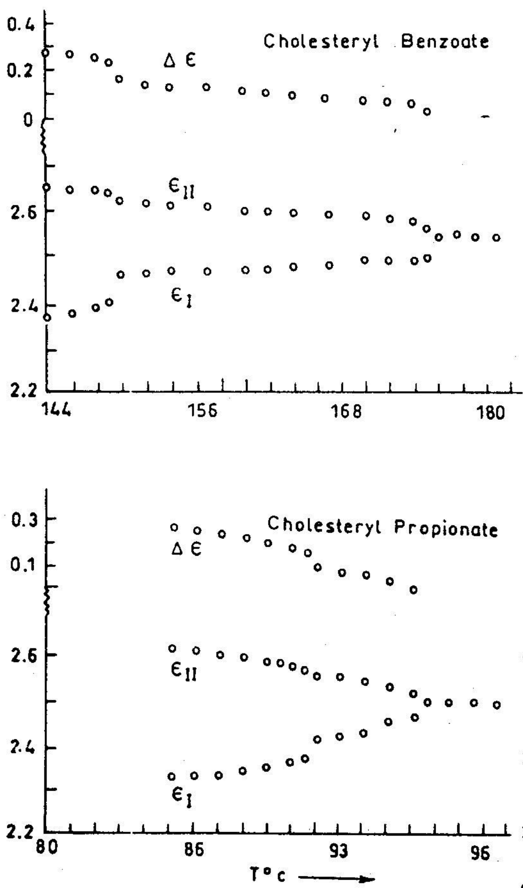

Fig. 1 - $\epsilon_{\perp}$, $\epsilon_{\parallel}$ and $\Delta\epsilon$ vs temperature for pure samples.

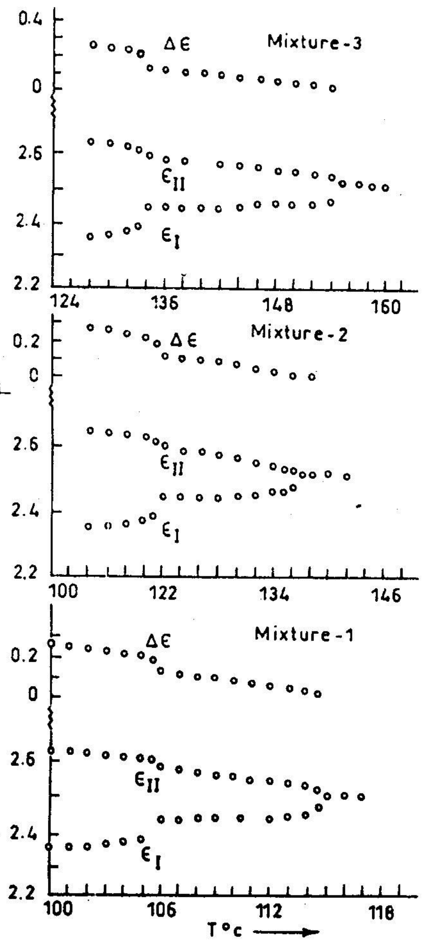

Fig. 2 - $\epsilon_{\perp}$, $\epsilon_{\parallel}$ and $\Delta\epsilon$ vs temperatue for mixture.

Fig. 2 shows variations of $\Delta\varepsilon$, $\varepsilon_{\parallel}$ and $\varepsilon\perp$ for the three homogeneous mixtures of the samples. It may be observed from these plots that the variation of all these parameters with temperature is similar to that of pure samples as explained above. The two transition temperatures, i.e., solid-cholesteric and cholesteric-isotropic, shift on the higher side with the increasing concentration of cholesteryl benzoate as shown in Table 1.

The dielectric losses (ε'') for all the samples at 20 kHz were quite small, lying within the range of error of measurements and hence not reported. Also no dielectric dispersion has been observed.

4.2 Optical Transmittance Measurement

The percentage optical transmittance for each sample was plotted against temperature during heating cycle. From Fig. 3 it may be seen that cholesteryl propionate shows a transition to cholesteric phase at 90°C. The percentage optical transmittance is higher in cholesteric phase than in the solid phase and it reaches 81% at 94.8°C. At this temperature it goes into isotropic phase and transmittance in this phase is quite high, i.e., nearly 94%. The transition temperatures are in good agreement with the values obtained using dielectric anisotropy study.

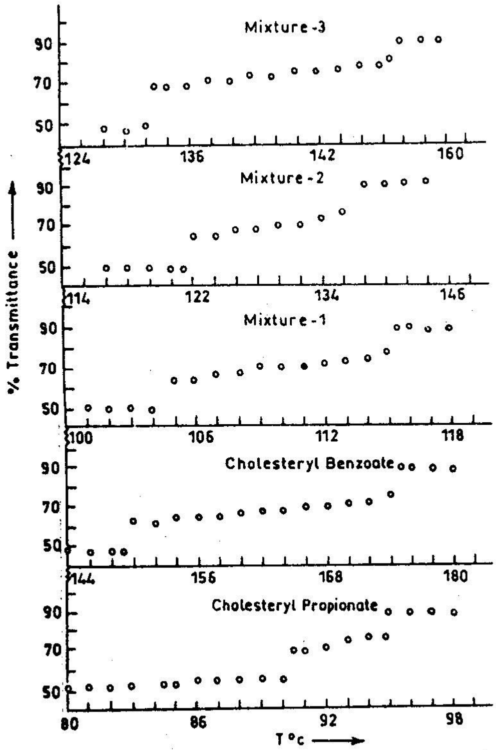

Fig. 3 - % Optical transmittance vs temperature for pure samples and mixture.

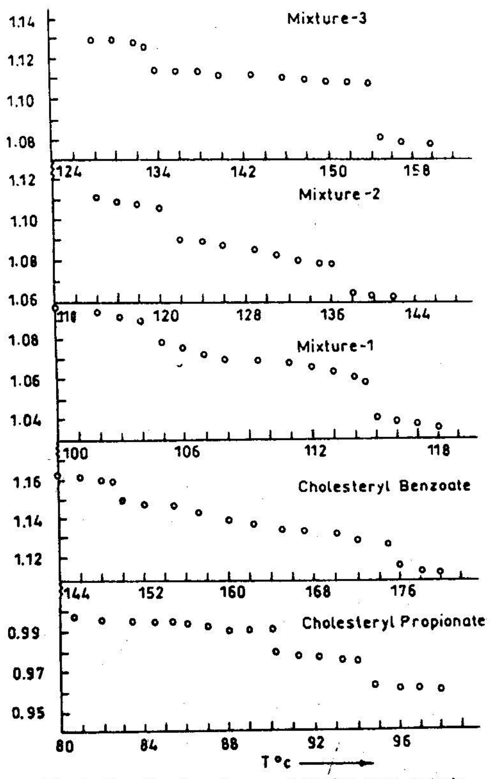

Fig. 4 - Density ρ vs temperature for pure sample mixture.

However, in the present study we are not able to detect the blue phase[12] as it appears for a very narrow range of temperature and very near to the Ch-I transition.

For cholesteryl benzoate, the S-Ch transition is observed at 149°C. Beyond this temperature the value of optical transmittance increases in cholesteric phase as has been observed for cholesteryl propionate. The transmittance attains a constant value of 93% once it goes into isotropic phase at 174°C.

The transmittance curve for mixture 1 (weight fraction 0.25) shows a sharp change at 104°C in optical transmittance indicating the S-Ch phase transition and the percentage optical transmittance at this temperature is 64%.

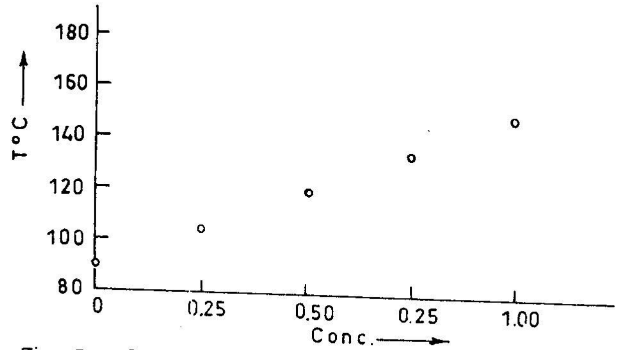

Fig. 5 – S-Ch transition temperature vs concentration of cholesteryl benzoate.

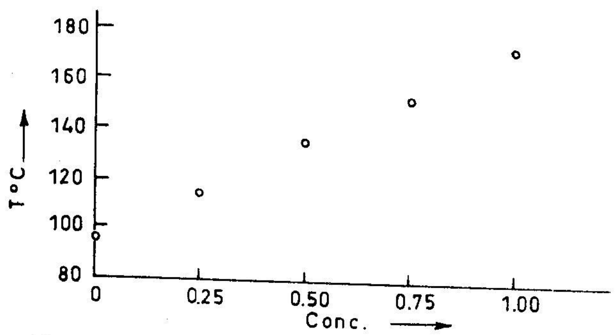

Fig. 6 – Ch-I transition temperature vs concentration of cholesteryl benzoate.

During cholesteric phase it increases and shows a jump at 115°C, indicating the Ch-I transition. For mixture 2 (weight fraction 0.50), the transition is at 121°C and transmittance at this temperature increases to 66% which is slightly larger than that for mixture 1. As the temperature is increased, the transmittance value registers a sudden rise at 136°C indicating the Ch-I phase transition. Mixture 3 (weight fraction 0.75), gives the S-Ch and the Ch-I phase transition at 132°C and 155°C, respectively, showing a further shifting of transition temperatures on the higher side for both the S-Ch and the Ch-I phase transitions. The transition temperature values obtained from optical transmittance study agree fairly well with those obtained by dielectric anisotropy study and density study given in Table 1.

Table 1 : Transition temperatures of pure samples and mixtures

Materials (wt. fraction)	Method	$T_{S\text{-}Ch}$ (°C)	$T_{Ch\text{-}I}$ (°C)
Cholesteryl propionate	Dielectric study	90.5	95
	Density	90	94
	Transmittance	90	94.8
	Literature value	92	96
Cholesteryl benzoyate	Dielectric study	149	175
	Density	149	175
	Transmittance	149	174
	Literature value	14	176
Mixture-1 (0.25)	Dielectric study	105.5	114.5
	Density	104	114.5
	Transmittance	104	115
Mixture-2 (0.50)	Dielectric study	121	136
	Density	120	136
	Transmittance	121	136
Mixture-3 (0.75)	Dielectric study	133	154
	Density	133	154
	Transmittance	132	155

4.3 Density Measurement

Density study has been used by some workers[13,14,15] to identify the transition in mesogens. The variation of density of these liquid crystals and their mixtures with temperature in the solid- cholesteric and the cholesteric-isotropic phase is shown in Fig. 4. The density changes are almost linear for all the samples under investigation except in the vicinity of the S-Ch and the Ch- I phase transition. The density value shows abrupt changes at both these phase transition points.

At solid to cholesteric transition, the density changes from 0.994 to 0.982 for cholesteryl propionate and from 1.160 to 1.151 for cholesteryl benzoate. The density value changes from 1.089 to 1.078 for mixture 1, from 1.106 to 1.092 for mixture 2 and from 1.120 to 1.115 for mixture 3 at S-Ch transition.

The change in the density at the Ch-I transition for cholesteryl propionate and cholesteryl benzoate are from 0.979 to 0.967 and from 1.130 to 1.119, respectively. For mixture 1, 2 and 3, the density changes from 1.060 to 1.044, from 1.080 to 1.065 and from 1.110 to 1.083, respectively. The observed transitions are indicated by discontinuities which suggest that these are first order transitions.

The variation of the S-Ch and Ch-I transition temperatures with concentration of cholesteryl benzoate in cholesteryl propionate are shown in Figs. 5 and 6, respectively. The variation of transition temperature with concentration are found to be linear. Similar linear variation of transition temperature with concentration were reported earlier also[16,17].

5. Conclusion

The measurement of dielectric anisotropy ($\Delta\varepsilon$), optical transmittance and density of cholesteryl benzoate and their three homogeneous mixtures show the S-Ch and the Ch-I phase transitions. The value of transition temperatures obtained by different techniques are in good agreement. The effect of mixing is also found as expected for the binary mixtures, i.e., the values of transition temperatures for both the S-Ch and the Ch-I transitions have been found to shift towards the transition temperature of cholesteryl benzoate with increasing concentration.

Acknowledgement

One of the authors (IB) is thankful to CSIR for grant of fellowship under JRF scheme.

References

1. P. G. de Gennes : The Physics of liquid crystals, Oxford University Press, Oxford, 1975.
2. S. Chandrasekhar : Liquid crystals, Cambridge University Press, Cambridge, *Rep. Prog. Phys.* (1977), **39** (1976) 613.
3. G. W. Gray : Advance in liquid crystals : Vol. **1**, Academic Press, N. Y. (1976).
4. M. Honciue, C. Motoc and O. Savin : *Mol. Cryst. Liq. Cryst.*, **95** (1983) 339.
5. E. F. Cart : *Cryst. Liq. Cryst.*, **13** (1971) 27.
6. W. Maier and G. Meier : *Z. Elektrochem*, **65** (1961) 556; *Z. Naturforsch*, **16a** (1961) 262.
7. A. Agrawal, V. P. Arora, R. V. Kaushik, P. P. Anand, V. K. Agrawal and B. Bahadur : *Indian J. Pure & Appl. Phys.*, **27** (1989).
8. L. Benguigui : *Phys. Rev.* **A-28**, (1983) 1852.
9. C. K. Shashidharan Nair and Kolluri, V. Ramanaiah : *Mol. Cryst. Liq. Cryst.* **103** (1983) 271.
10. R. T. Khingbiel, D. J. Genova and H. K. Bucher : *Mol. Cryst. Liq. Cryst.* **27** (1974) 1.