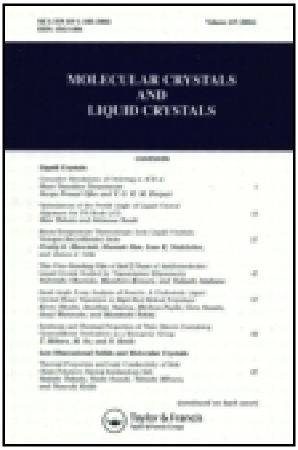

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Refractive Indices, Order Parameter and Principal Polarizability of Cholesteric Liquid Crystals and Their Mixtures

Abhishek Kumar Srivastava [a] , Rajiv Manohar [a] & J. P. Shukla [a]

[a] Physics Department, University of Lucknow, Lucknow, India

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Refractive Indices, Order Parameter and Principal Polarizability of Cholesteric Liquid Crystals and Their Mixtures

Abhishek Kumar Srivastava
Rajiv Manohar
J. P. Shukla
Physics Department, University of Lucknow, Lucknow, India

Measurements of refractive indices (n_e, n_o) and birefringence (Δn) have been made in solid, cholesteric and isotropic phases of cholesteryl carbonate, cholesteryl stearate and their three homogeneous mixtures of concentration 0.25, 0.50 and 0.77 at varying temperature in the range of 18°C to 35°C. the results clearly indicates that various transitions are of the first order. For accurate measurement of Δn, a modified wedge method was used. Using n_e and n_o, principal polarizability (α_e, α_o), internal field factor (γ_e, γ_o) and order parameter (S) have been evaluated, and their temperature dependence is discussed. The order parameter has been determined using the isotropic internal field model (Vuks approach) and the anisotropic internal field model (Neugebauer's approach), and both values agree up to average deviation of 0.7%.

Keywords: birefringence; cholesteryl carbonate; cholesteryl stearate; liquid crystal mixtures

1. INTRODUCTION

The order parameter (S) [1–5], of a liquid crystal is among the most important parameters which govern all its physical properties. The macroscopic order parameter (Q) [1–3], can be determined by any bulk tensorial property like electric and magnetic susceptibilities, elastic constants, refractive indices etc. However, the microscopic order parameter (S) is defined as $S = 1/2\langle 3\cos^2\theta - 1\rangle$ where θ is the angle between long axis of the molecule and director [4]. The macroscopic

Address correspondence to Abhishek Kumar Srivastava, Physics Department, University of Lucknow, Lucknow, 226007, India. E-mail: abhishek_srivastava_lu@yahoo.co.in

order parameter as determined from the help of different bulk tensorial properties differs among themselves and also from the microscopic order parameter [1–6] because the effect of a local field is different for different properties. But from the knowledge of macroscopic bulk tensorial properties microscopic order parameter can be determined just by assuming the validity of a given local field model [1–6]. Various tensorial properties like dielectric properties, its anisotropy, viscosity etc. have been studied in the past but the optical anisotropy i.e. measurement of Δn provides one technique which yields a direct and fairly accurate value of microscopic order parameter (S) in comparison to those obtained from the use of other properties. During the past few years the order parameter of large number of nematic liquid crystals has been reported using optical anisotropy data [6–11]. However, some studies also report dielectric anisotropy, conductive anisotropy, optical anisotropy and order parameter of aligned cholesteric liquid crystals and their mixtures [12–15]. Shivaprakash *et al.* [12] have been reported optical anisotropy data of aligned cholesteryl benzoate. Binary mixtures of aligned cholesteryl chloride and cholesteryl alkanoates have been studied by C. K. Sasidhar Nair *et al.* [13] for cholesteric-nematic transformation induced by electric field. Dielectric permittivity and electric conductivity anisotropy of cholesteryl laurate and cholesteryl caprilate have been reported by Honciuc *et al.* [14]. Smectic or nematic are normally optically positive with $n_e > n_o$. In the present work we have taken two optically negative crystals and also their three homogeneous mixtures of concentrations 0.25, 0.50, and 0.77. We have measured refractive indices (n_e, n_o) and using these values, the order parameter (S), principal polarizability (α_e, α_o), and internal field factor (γ_e, γ_o) have been determined. The density values which are essential for determination of order parameter have been used from our earlier reported work [16].

2. EXPERIMENTAL DETAILS AND THEORY

The refractive index (n), of a liquid crystal can be determined easily and accurately using an Abbe's refractometer in its isotropic phase (with an accuracy of 0.1%). However, as the material is anisotropic in other phases, the study of birefringence becomes necessary as a fundamental property. The ordinary refractive index (n_o) and extraordinary refractive index (n_e) can be determined normally by Abbe's refractometer with the addition of a properly polarized polarizer to block one of the rays, i.e., ordinary or extraordinary. Then, by changing the position of polarizer by 90° the refractive index can be determined. But, whenever one of the refractive indices is out of the range of

Abbe's refractometer (1.3 to 1.7), some other technique has to apply. In the present work the samples used are cholesteric liquid crystals which are optically negative [12,17] i.e., $n_o > n_e$. The method used to determine a higher refractive index (above the upper limit of the range of Abbe's refractometer) in the present work is wedge method [6,10] modified by Saran *et al.* [18–20].

The sample-filled wedge is formed by these aligned plates as described by Saran *et al.* [18–20]. The temperature of the sample was varied by placing the wedge in a specially designed double-walled chamber with circulating water from a refrigerated thermostat. The temperature was measured within an accuracy of ±1°C.

The order parameter can be expressed as:

$$S = \frac{\alpha_e - \alpha_o}{\alpha_{\|} - \alpha_{\perp}}$$

where α_e and α_o are the principal polarizabilities in mesomorphic phases $\alpha_e - \alpha_o$ are principal molecular polarizabilities. $\alpha_{\|} - \alpha_{\perp}$ is assumed to be equal the value of $\alpha_e - \alpha_o$ at absolute zero [6] and is obtained by extrapolating $(\alpha_e - \alpha_o)$ vs. $(T - T_c)$ curve at $T = 0°C$.

To determine α_e and α_o from n_e, n_o it is necessary to know the nature of local field, particularly its anisotropy. If it is assumed that local field is isotropic (Vuks approach) [21,22], we have

$$\alpha_{e,o} = \frac{3}{4\pi\pi}\frac{n_{e,o}^2 - 1}{\bar{n}^2 + 2} \tag{1}$$

$$\bar{n}^2 = \frac{n_e^2 + 2n_o^2}{3}$$

where N is number of molecules per cm^3.

$$N = \frac{N_A \rho}{M}$$

N_A is Avogadro's number, ρ, the density and M, molecular weight.

If, however, local field is anisotropic, one can use Neugebauer's relation [23,24].

$$n_{e,o}^2 - 1 = \frac{4\pi\ N\alpha_{e,o}}{1 - N\alpha_{e,o}\gamma_{e,o}} \tag{2}$$

where γ_e and γ_o are internal field factors $\gamma_e + 2\gamma_o = 4\Pi$.

For a single crystal of known crystal Structure it is possible to determine internal field factor, α_e and α_o by this method. However, for liquid crystals, as the order parameter is temperature dependent, the γ_e and γ_o will also be temperature dependent. Equation (2) may be written as

$$\frac{1}{\alpha_e}+\frac{2}{\alpha_o}=\frac{4\pi N}{3}\left(\frac{n_e^2+2}{n_e^2-1}+\frac{2n_o^2+2}{n_o^2-1}\right) \tag{3}$$

In the isotropic phase

$$\gamma_e=\gamma_o=4\gamma/3 \quad n_e=n_o=n, \quad \text{and} \quad \alpha_e=\alpha_o=\alpha$$

Assuming that α remains same in all the phases, we have

$$\alpha_e+2\alpha_o=\alpha_{\|}+\alpha_{\perp}=\frac{9}{4\pi N}\left[\frac{n^2-1}{n^2+2}\right] \tag{4}$$

where N_i is the no. of molecules per cm^3 in the isotropic phase. α_e and α_o can be determined from Eqs. (2) and (3). Thus knowing the value of α_e and α_o, S can be determined and γ_e, γ_o can be determined from Eq. (2).

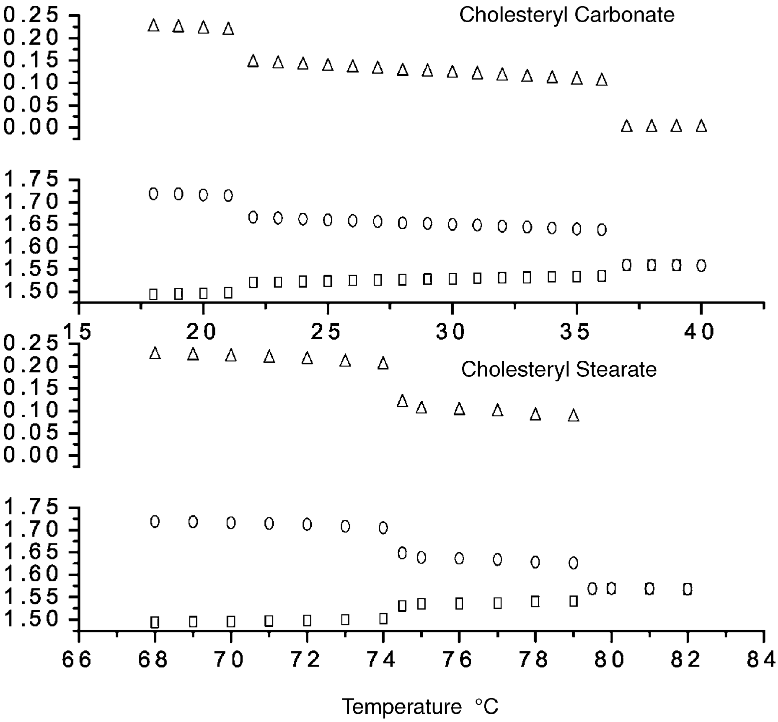

FIGURE 1 Variation of n_o (○), n_e (□), and Δn (△) with temperature for pure samples.

3. RESULTS AND DISCUSSION

The variation of ordinary and extraordinary refractive indices (n_o, n_e) and the birefringence (Δn) with temperature for cholesteryl carbonate and cholesteryl stearate, is given in Figure 1.

For cholesteryl carbonate, the observed birefringence value is nearly 0.23 in the solid phase and indicates a sudden drop at 21°C, indicating the solid-cholesteric transition. After 21°C, the Δn values decreases gradually with the temperature in the cholesteric phase and reaches nearly 0.12 at Ch-I transition point at 36°C. The higher value of Δn in solid phase is due to increased orderedness, which results in increase in anisotropy. The curves of n_o and n_e also shows transition at the same point as shown by Δn curve. The value of n_o is greater than n_e as the cholesteric crystals are uniaxial and optically negative [12,17]. Similarly for cholesteryl stearate Δn value decreases

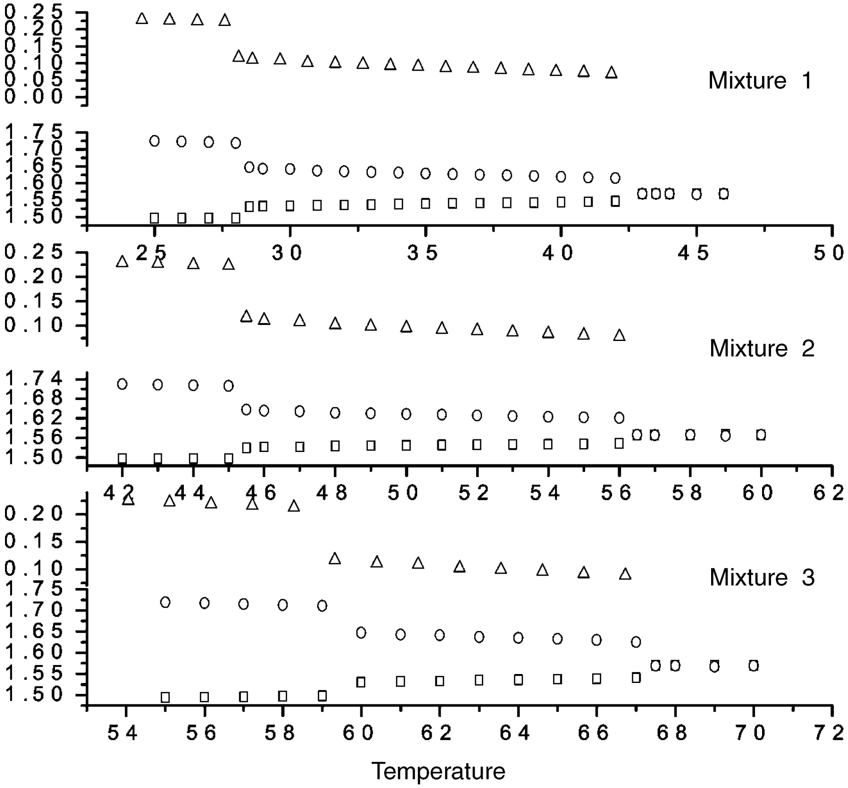

FIGURE 2 Variation of n_o (○), n_e (□), and Δn (△) with temperature for mixtures.

very slowly in the solid phase and an abrupt change occurs at 74°C indicating S-Ch transition. In the cholesteric phase Δn decreases much faster than the cholesteryl carbonate and at Ch-I transition its value is slightly less than 0.12. In the isotropic phase refractive index (n) decreases slightly with an increase in temperature like any other normal organic liquid [25].

For three homogeneous mixtures of different concentration (0.25, 0.50, 0.77) the values of refractive indices (n_o, n_e) and birefringence (Δn) has been plotted with temperature in Figure 2. For all the three mixtures these parameters change almost in the same manner as in pure samples in the solid and isotropic phases. However, in the cholesteric phase, the Δn value decreases much more sharply as the concentration of cholesteryl stearate is increased. For mixture I (0.25) the two transitions are noticed at 28°C and 43°C and Δn decreases from 0.18 to 0.11 in the cholesteric phase. The values of n_o and n_e also show abrupt changes at these transition points which is exhibited from the Figure 2. Similarly for mixture II (0.50) Δn decreases from 0.22

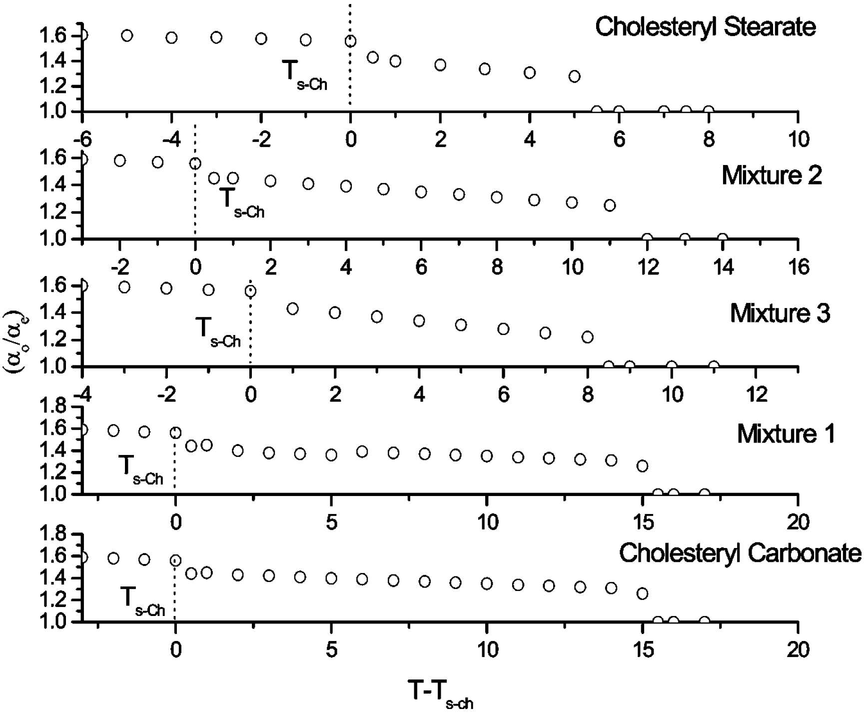

FIGURE 3 (α_o/α_e) vs. S T − T_c for pure samples and their three mixtures.

to nearly 0.18 indicating S-Ch transition at 45°C and it further decreases with increase in temperature and reaches a value of 0.11 giving Ch-I transition at 56°C. For mixture III (0.77) the two transition temperatures obtained are at 59°C and 67°C, which is shown by discontinuities in Δn, n_e and n_o curves with temperature. The two transition temperatures also exhibit shifting towards the higher side with the increasing concentration of cholesteryl stearate.

The values of transition temperatures obtained by a study of n_o, n_e, and Δn also show that the shifting of the two transition temperatures agree fairly well with those obtained using dielectric, density and optical transmittance study for all the samples reported in our earlier work [16].

The temperature variation of (α_o/α_e) for both pure samples cholesteryl carbonate and cholesteryl stearate and their three mixtures are given in Figure 3. The ratio of the two principal polarizabilities (α_o/α_e) increases gradually with decreases in temperature, but near Ch-S transition (α_o/α_e) value increases sharply to a higher value for all samples. This sudden increase in the value (α_o/α_e) at Ch-S

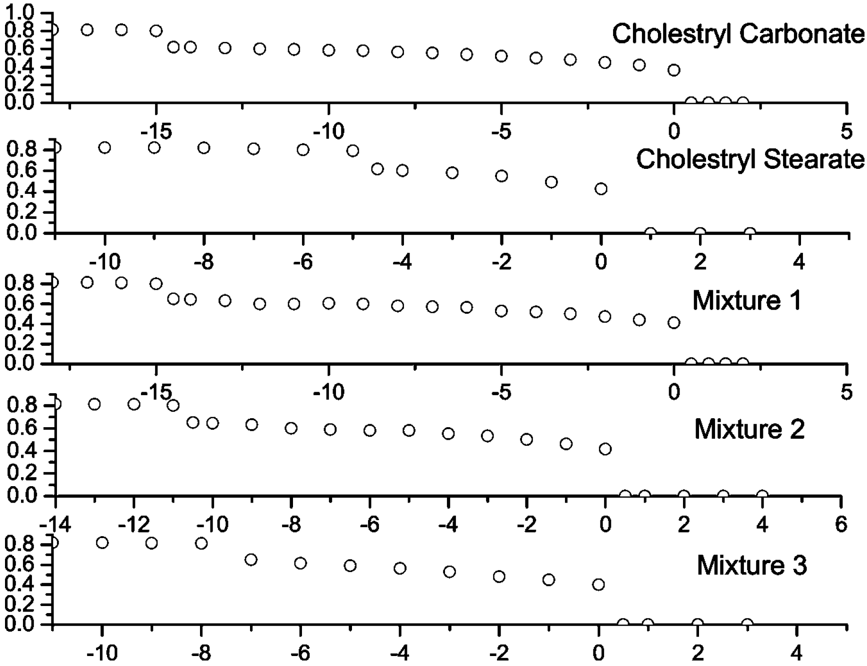

FIGURE 4 Order parameter vs. $(T - T_{Ch\text{-}I})$°C for pure sample and mixtures (Vuks approach).

transition shows that anisotropy increases in solid phase than in cholesteric phase because solid phase is much more ordered. Values of (α_o/α_e) in the isotropic phase for all the systems are dependent upon the variation of (α_o/α_e) which themselves depends on two factors:

1. Variation of order parameter which is related to the orientation of long molecular axis with respect to the director.
2. Buckling of end alkyl groups in the molecules. This buckling increases with increases in temperature and consequently reduces the (α_o/α_e) ratio.

Higher values of (α_o/α_e) in the solid phase as compared to the cholesteric phase in all the cases indicate that the solid phase is more ordered than the cholesteric phase and thus molecular chain is much more rigid [18].

The variation of the order parameter (S) with temperature is shown in Figures 4 and 5 as determined by isotropic field model using Vuks relation [21,22] and by anisotropic local field model using Neugebauer's relation [23,24].

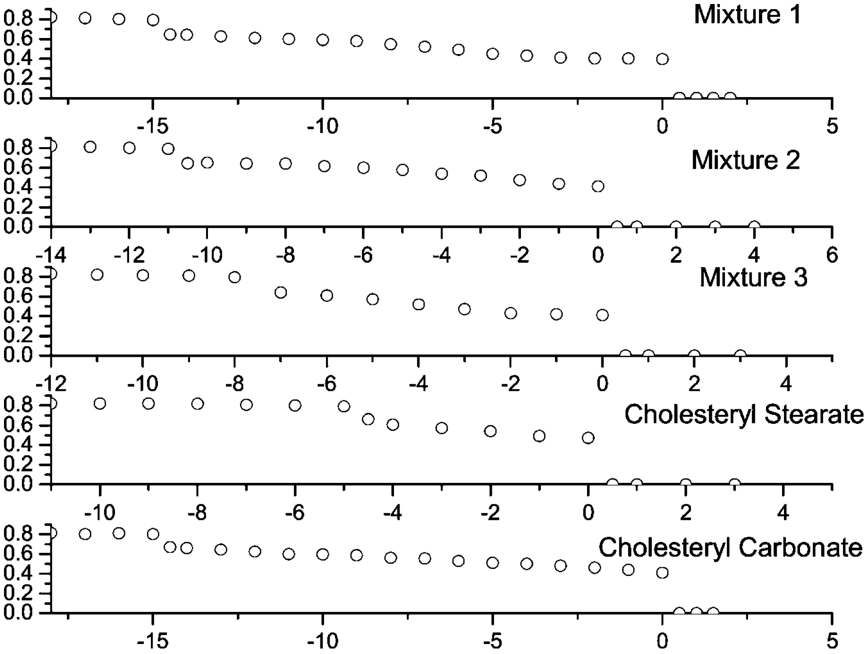

FIGURE 5 Order parameter vs. $(T - T_{Ch\text{-}I})$°C for pure sample and mixtures (Neugebauer's approach).

For all the samples S is fairly constant in solid phase and decreases sharply at S-Ch transition with increase in temperature. Thereafter S decreases gradually with increase in temperature. Thereafter S decreases gradually with increasing temperature until Ch-I transition temperature is reached after which S becomes zero. This is expected because the isotropic phase is completely disordered. The temperature dependence of S is higher in cholesteric phase than in solid phase. The variation of S as described above is valid whether isotropic field model or anisotropic field model is used.

It may be seen that that order parameter computed from optical anisotropy data using the isotropic field model (Vuks approach) and the anisotropic field model (Neugebauer's approach) agrees well and the average deviation is found to be 0.7% for both liquid crystals and their mixtures in all phases. The agreement in the values of the order parameter calculated from two approaches may appear strange but it is due to the fact that the order parameter is the ratio of $(\alpha_o - \alpha_e)$ to $(\alpha_{\|} - \alpha_{\perp})$. So, although α_o and α_e are sensitive to the nature of local field, this ratio is independent of the model [24]. A slight variation in the solid phase is due to the fact that the anisotropy is considerable in this phase. It appears from the results that Neugebauer's approach is more realistic than Vuks approach as it includes the fact that local field is anisotropic in nature.

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