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Order Parameter and Refractive Index of Cholesteryl Linoleate

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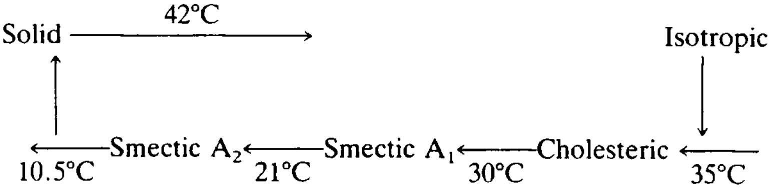
Refractive indices of cholesteryl linoleate are determined at different temperatures and order parameters have been calculated in smectic and cholesteric phases.

INTRODUCTION

A large fraction of biological and pathological systems contain cholesteryl esters. Cholesteryl oleate (CO), cholesteryl linoleate (CL) and cholesteryl linolenate (CLn) form a large part of lipoproteins and the lipid of lesions of atherosclerosis. The phase behaviour of these esters have been studied by Small et al.[1-3] The dielectric behaviour of CL has been studied by Gupta et al.[4] Dubini et al.[5] have studied the phase transitions of CL recently. In this paper we discuss the order parameters in smectic and cholesteric phases on the basis of the refractive index data of CL.

EXPERIMENTAL

The compound was obtained from M/s Eastman Kodak Co., and was used without further purification. The transition thermograms were recorded on Perkin-Elmer DSC-2 Scanning Calorimeter. From the thermograms, optical observations and X-Ray studies following transition temperatures were obtained:



Smectic A_2 phase of closer packing has been found to be formed while cooling below 21 °C, from our recent X-Ray investigations.[6] The refractive indices of the compound were determined at different temperatures using Abbe's Refractometer. The measurements were made in smectic (A_1) and cholesteric phases during cooling and reheating of the cooled sample. The refractive indices for the ordinary ray (n_o) and the extraordinary ray (n_e) were calculated using Vuk's formula.[7,8] Figure 1 is a plot of n_e, n_o and Δn with temperature.

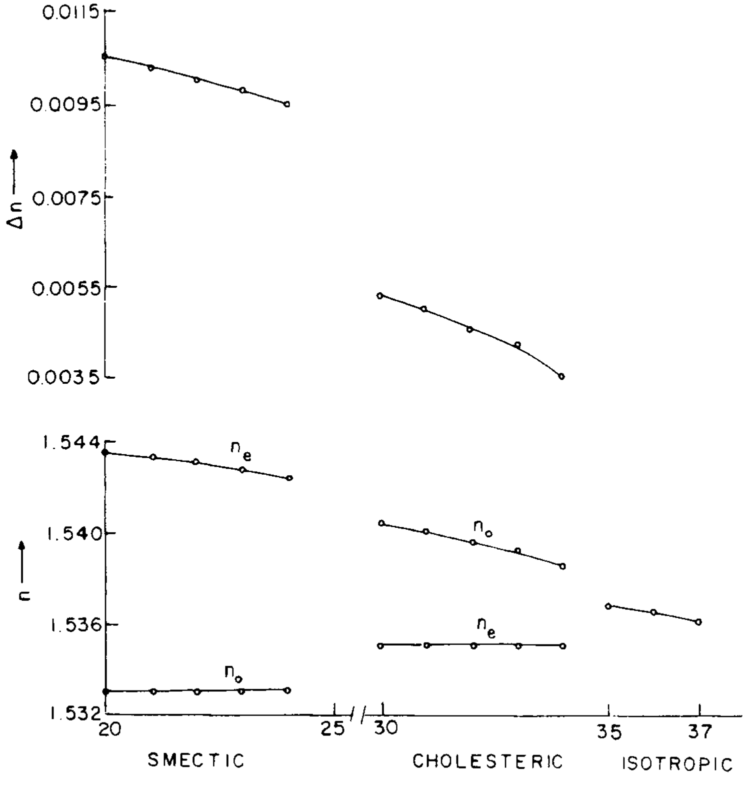


FIGURE 1 Plot of n_e, n_o and Δn against temperature.

It has been shown that the method of bond polarizability gives an accurate value of the mean polarizability.[9] It is also established that the Lippincott-δ-Function method can be used to determine the mean polarizability of long chain molecules. Therefore the mean polarizability for CL was determined by bond polarizability and Lippincott-δ-Function methods.[10-12] These values agree very well.

CALCULATION OF ORDER PARAMETER

The order parameter in the smectic (A_1) phase was calculated using Neugebauer's relations[13,14]

$$n^2_{e,o} - 1 = 4\pi N\alpha_{e,o}/(1 - N\alpha_{e,o}\gamma_{e,o}) \tag{1}$$

where γ_e and γ_o are the internal field factors and $\gamma_e + 2\gamma_o = 4\pi$. In the liquid crystalline phase the internal field factors are temperature dependent as the order parameter changes with temperature. With the knowledge of $\bar{\alpha}$ (from bond polarizability and Lippincott-δ-Function methods) α_e and α_o are calculated at different temperatures. Extrapolation of the plot of $\log[\alpha_e/\alpha_o]$ vs. $\log[T - T_c]$ gives the value of $\alpha_{\parallel} - \alpha_{\perp}$ and S is determined using the relation

$$S = \frac{\alpha_e - \alpha_o}{\alpha_{\parallel} - \alpha_{\perp}} \tag{2}$$

Figure 2 is a plot of α_e/α_o and γ_e against temperature. Averyanov and Shabanov's relation[15,16] was used to calculate the order parameter in the cholesteric phase. The order parameter (S) is given by the relation

$$S = \frac{3M\,[n_{\parallel} + n_{\perp}]\,\Delta n'}{2\pi N_A \rho[\bar{n}^2 + 2]\,\Delta\gamma} \tag{3}$$

where M is the molecular weight, $\Delta n' = -\Delta n$, N_A is Avegadro number, ρ is the density, $\Delta\gamma$ the mean molecular polarizability anisotropy. Rewriting the relation (3) in terms of mean polarizability ($\bar{\alpha}$)

$$S = \frac{2\bar{\alpha}[\,n_{\parallel} + n_{\perp}\,]\,\Delta n'}{[\,\bar{n}^2 - 1\,]\,\Delta\gamma} \tag{4}$$

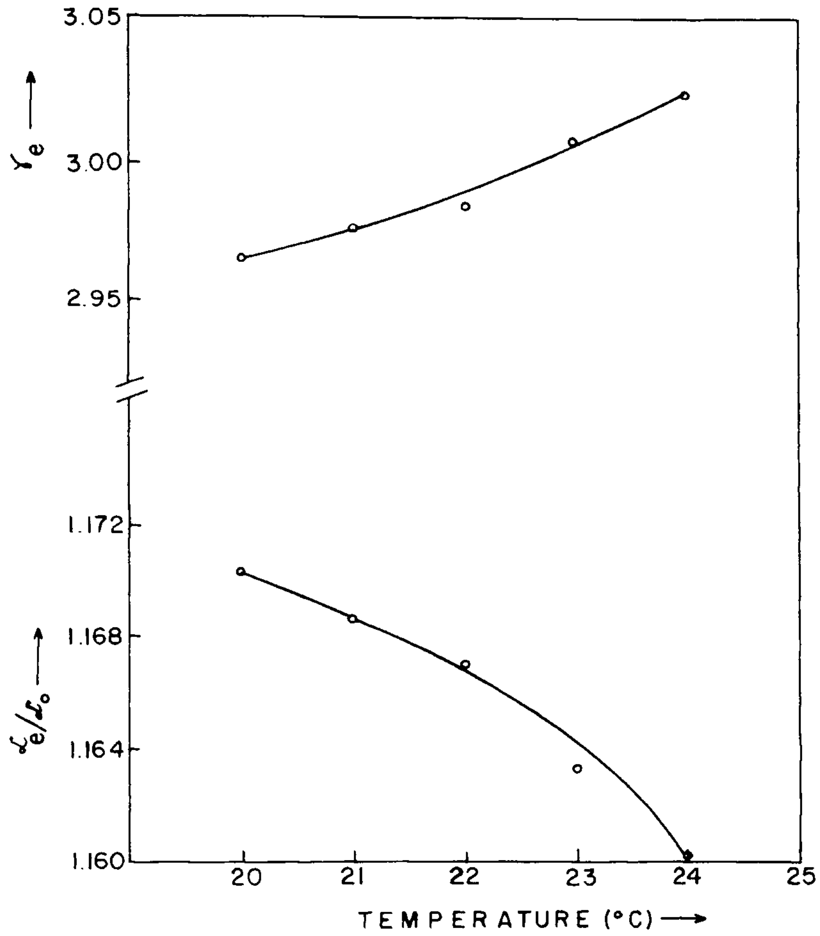


FIGURE 2 Plot of α_e/α_0 and γ_e the internal field factor against temperature.

Figure 3 is a plot of log $S\Delta\gamma$ against log$(1 - T/T^*)$, where dependence is seen to be linear. Assuming that at $T = 0$, $S = 1$ and by extrapolating the straight line in Figure 3, we can obtain the value of effective molecular polarizability anisotropy ($\Delta\gamma_0 = 5.73 \times 10^{-24}$ cm^3). Order parameter was calculated using the value of $\Delta\gamma_0$. Values of order parameter (S) obtained fit within the equation $S = S_0(1 - T/T^*)^\eta$, ($\eta = 0.25$). Figure 4 is a plot of order parameter (S) against T/T^* in smectic and cholesteric phases.

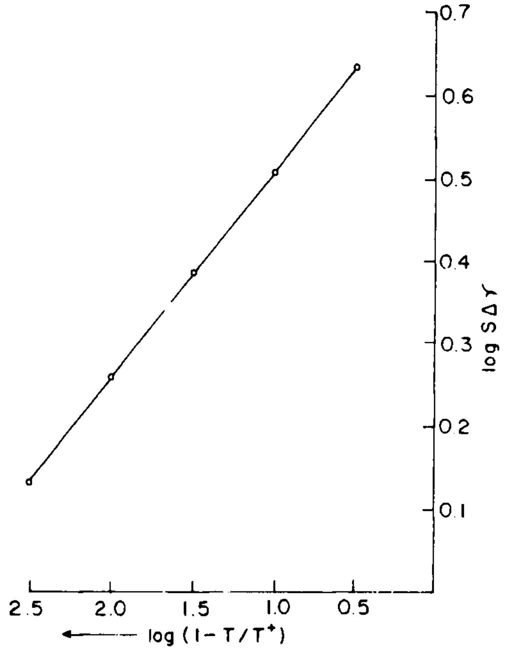


FIGURE 3 Plot of log $S\Delta\gamma$ against $\log(1 - T/T^*)$.

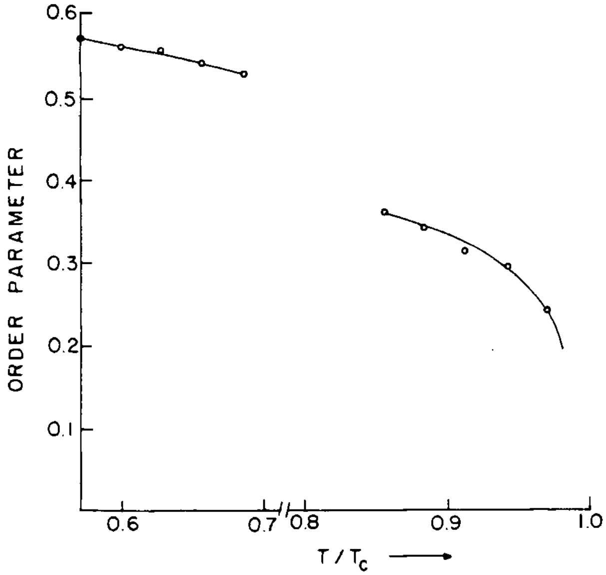


FIGURE 4 Plot of order parameter (S) against T/T^* in smectic and cholesteric phases.

RESULTS AND DISCUSSION

CL transforms itself into smectic A_2 phase at 21°C from the smectic A_1 phase and on further cooling transforms into solid at 10.5°C. It has been found that the intermolecular distance within a layer decreases and inter layer distance increases in smectic A_2 phase. On heating the smectic A_2 phase, the conformational and thermal disordering of the linoleate chains are exaggerated and the cholesteric–cholesteric interaction weakens giving rise to very low order parameter in the smectic A_1 phase. α_e/α_o decreases and the internal field factor (γ_e) increases, signifying that the molecules attain greater freedom and therefore the order parameter decreases as the temperature increases.

Figure 5 is an approximate model of molecular structure of CL. The kink formed at two double bonds (C_9–C_{10} and C_{12}–C_{13}) appears to be greater than the kink formed in the CO chain and the last four members (C_{15}–C_{18}) appear to be lying in a different plane. Krishnamurti et al.[17] have shown that the buckling of end alkyl groups increases with increase in temperature and thus reducing the value of α_e/α_o. The presence of two unsaturated bonds in the CL chain limits the buckling to last four members (C_{15}–C_{18}). Hence it appears that the reduction in α_e/α_o is more due to the reduction in the order parameter (i.e., increase in θ, the preferred direction) than due to buckling of end chain in this compound.

The order parameter (S) in the cholesteric phase decreases very rapidly with increase in the temperature, compared to the decrease in the smectic phase and also the value is very much lower in the cholesteric phase than in the smectic phase. The range for S for nematic liquid crystalline compounds is 0.3–0.7.[18–22] Hence the results obtained in this work for smectic and cholesteric phases are in accordance with the values in the literature.[17–22]

The value of mean molecular polarizability anisotropy ($\Delta\gamma_0$) is less than the value obtained for other cholesteric compounds[15] and also the value of the exponent η in the relation $S = S_0(1 - T/T^*)^\eta$ obtained by us is very much greater than the values obtained[15] for other cholesteric compounds. This may be attributed to the presence of two double bonds in the linoleate chain. The C–C bonds from C_1–C_9 appear to be in the plane of the sterol ring system. This increases the rigidity of the chain of the molecules and hence the anisotropy decreases compared to other cholesteric molecules where the end chains are more flexible. η is a measure of the rate of change of the orientational order with respect to the temperature. Greater rigidity

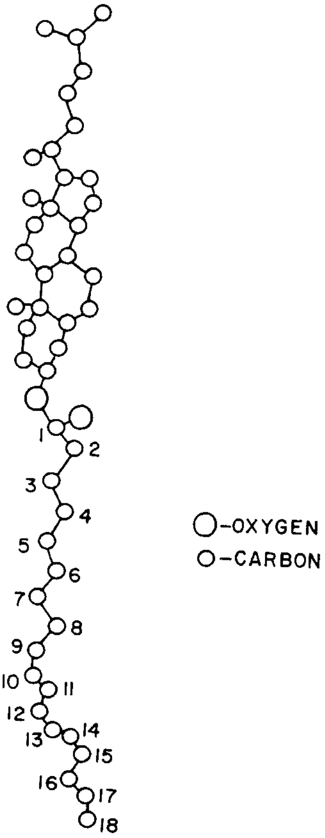


FIGURE 5 An approximate model of the cholesteryl linoleate molecule.

and asymmetry[23] of the molecule contribute to the greater rate of change in the orientational order parameter in this compound.

CONCLUSIONS

Very low value of the order parameter in smectic A_1 phase indicates that the molecules are very loosely packed together in that phase. Increased rigidity of the molecule due to the presence of two unsaturated bonds causes a steep fall in the order parameter of the cholesteric phase. Experiments are in progress to identify correctly the additional smectic phase (smectic A_2) formed during cooling below 21°C.

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