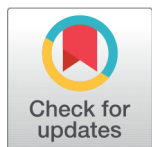


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Principal Polarizability and Orientational Order Parameter Study of some Pure Cholesteric Liquid Crystals and their Homogeneous Mixtures: Phase Transition Behaviour

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Abstract

Objectives: To study the behavior of the molecular polarizabilities (α_e , α_o) and order parameter (S) in various phases of Cholesteryl Propionate, Cholesteryl Benzoate and their homogeneous mixtures of weight fractions 0.25, 0.50 and 0.75. **Methods:** The measurement of extraordinary refractive index (n_e) and ordinary refractive index (n_o) was carried out with the help of Abbe's refractometer and modified wedge method, in the temperature range of 85^oC–180^oC. The anisotropic internal field model is used to calculate the internal field factor (a) and order parameter (S). **Findings:** The decrease in the ratio of the principal polarizabilities (α_o / α_e) with increase in temperature has been observed. At the transition points of solid to cholesteric (S-Ch transition) and cholesteric to isotropic (Ch-I transition), the decrease in the ratio of principal polarizabilities is much sharper for both Cholesteryl Benzoate and Cholesteryl Propionate and also for their mixtures. The value of the order parameter (S) remains constant in solid phase and sharp decrease occurs in its values for pure samples as well as their mixtures, when materials go from solid to cholesteric phase (S-Ch transition). After the S-Ch transition, the order parameter (S) goes on decreasing with further increase in temperature until the cholesteric to isotropic transition (Ch-I transition) occurs. **Novelty:** Some researchers have calculated the principal polarizabilities and order parameter of optically positive nematic liquid crystals and aligned cholesteric liquid crystals by using isotropic internal field model such as Vuk's approach. This itself raises the question of how can an anisotropic environment give rise to isotropic field. The present study is based on the anisotropic field model suggested by Maier and Saupe in which the internal field acting on a molecule is considered to be anisotropic. This approach used to calculate principal polarizabilities and order parameter is more realistic and gives more accurate results.

Keywords: Cholesteric; Isotropic; Birefringence; Polarizability; Order Parameter; Anisotropic Internal Field Factor

1 Introduction

In recent years, the quest for the new materials having novel properties that can meet the day-by-day increasing technological demands has also revolutionized the research in the field of Liquid Crystals (LCs). This has given rise to a new approach called ‘Guest – Host’ approach where LC materials (the Host) are doped with some other materials (the Guest) like dyes, polymers, nanomaterials etc. to manipulate the inherent properties of these materials so that a new material can be synthesized that can fulfill the need as per the required specifications⁽¹⁻⁴⁾. Though this approach is very much in demand and is fulfilling its purpose, one area which can also produce some novel materials is the mixing of one LC with another one with different amount of concentrations as it can significantly alter the properties of materials⁽⁵⁾.

Mixing of two or more liquid crystals makes it possible to prepare new materials as per the requirement because the intermolecular interaction between the two mesomorphic phases can greatly influence the optical anisotropy of both^(6,7). Further, for practical applications, those liquid crystals are preferred that not only shows their mesomorphic phase at room temperature but also maintains it for a long temperature range.

Cholesteric Liquid Crystals (CLC) were the first liquid crystals discovered by Friedrich Reinitzer in 1888 and since then they have played a significant role in redefining the various technologies related to optics and nanomaterials⁽⁸⁾. These liquid crystals, which are also known as Chiral Nematic, have a helical director along which the molecules orient themselves in helical order. The optical properties of these CLCs become prominent when the pitch of this helical director becomes comparable to the wavelength of visible light. This gives rise to application of these CLC in lasing devices, photonic band gap devices, tunable reflectors, light shutters, optical filters to name a few⁽⁹⁾. Anisotropic optical properties also play a key role in the applications of CLCs as they give an idea about the thickness of the liquid crystal layer in display devices⁽¹⁰⁾.

Generally, the CLCs are birefringent i.e. their refractive indices are different along and perpendicular to the optic axis⁽¹¹⁾. With the rise in temperature, the birefringence goes on decreasing and becomes zero when the transition from cholesteric phase to isotropic phase takes place. The birefringence study helps in determining one of the most important parameters of CLCs, called ‘Order Parameter’. The importance of the order parameter lies in the fact that almost all the properties of a liquid crystal depend on it, whether they are in pure form or in mixed form. The changes in order parameter with temperature are also important from the technological point of view. The CLCs with low values of birefringence and higher values of order parameter are considered good for practical applications⁽¹²⁾,⁽¹³⁾.

The microscopic order parameter gives the information regarding the molecular alignment about the director and is given as -

$$S = \frac{1}{2} \langle 3 \cos^2 \theta - 1 \rangle$$

where $\langle \rangle$ denotes average behavior of θ with temperature (thermal averaging) and θ denotes the angle between the molecular axis and director. The value, $S = 1$ represents the perfect alignment whereas $S = 0$ denotes the random alignment of molecules with the director that exist in isotropic liquid. So, higher values of order parameter represent the more ordered phase of a liquid crystal.

Though a lot of studies have been done in the past to characterize the order parameter of a large number of optically positive ($n_e > n_o$) nematic and cholesteric materials by studying their optical anisotropy and barring a few studies on LC mixtures, very limited data is available on the optically negative CLCs and their mixture of homogeneous composition. Also, the objective of mixing the LCs in different concentrations to tune the transition temperature is rarely described in literature.

Here, we report the tuning of transition temperatures by studying the microscopic order parameter (S) from molecular polarizability and optical anisotropy of optically negative ($n_e < n_o$) CLCs namely Cholesteryl Propionate, Cholesteryl Benzoate and their three homogeneous mixtures. For this purpose, Maier and Saupe’s anisotropic internal field model have been taken into account because this method provides direct and reasonably accurate value of the order parameter.

2 Methodology

The materials were procured from Merck, Germany and were used as such without any further purification. The various steps involved in the calculation of order parameter using the optical anisotropy data are as under –

- Measurement of both ordinary (n_o) and extraordinary (n_e) refractive indices.
- Measurement of density (ρ).
- Calculation of optical anisotropy ($\Delta n = n_e - n_o$)
- Determination of molecular polarizabilities (α_e and α_o) from optical anisotropy data.
- Calculation of order parameter (S) from molecular polarizabilities.

Abbe’s refractometer (range 1.3 – 1.7) was used to measure the refractive index (n) in the isotropic phase of samples. Since the CLC samples used in this study are anisotropic, the birefringence study was also carried out for measurement of n_e and n_o

till their values lies within the range of refractometer. This was done by attaching a polarizer to refractometer and blocking one of the rays and then rotating the polarizer by 90⁰C from initial position. When the values of refractive indices were higher than the range of refractometer, a modified wedge method was used⁽¹⁴⁾. All the measurements were done in the temperature range 85⁰C – 180⁰C. Optical anisotropy (Δn) has been determined by the relation

$$\Delta n = n_e \sim n_o \tag{1}$$

For density measurements in cholesteric and isotropic phases, the capillary rise method was used by placing a sample filled glass capillary tube in a thermostat. The sample length in a capillary tube at different temperature was measured by a travelling microscope. After correction for expansion of glass tube, the density was calculated⁽¹⁵⁾.

The principal polarizabilities (α_e, α_o) were calculated using Maier and Saupe’s method and their values were used to calculate the values of order parameter (S)⁽⁶⁾. The expression relating order parameter to principal polarizabilities is⁽¹⁶⁾

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

where α_e and α_o are principal polarizabilities in mesogenic phase and V/s (T – T) graph at 0⁽¹⁷⁾.

In the present work, Maier and Saupe’s approach has been used to calculate the α_e and α_o values. This approach is applicable when the internal field is anisotropic. In this approach, a single internal field constant ‘a’ is assumed, whose value can be calculated from the relation-

$$\left(\frac{n^2 - 1}{n^2 + 2}\right) V_{iso} = \frac{1}{3} \left[\frac{n_c^2 - 1}{n_c^2 + 2 - 2a(n_c^2 - 1)} + \frac{n_v^2 - 1}{n_c^2 + 2 + a(n_v^2 - 1)} \right] V_{ch}$$

where V_{iso} and V_{ch} are molar volumes in isotropic and cholesteric phases respectively.

$$\alpha_e = \frac{3}{4\pi N} \left[\frac{1}{1 - a + \frac{3}{n_e^2 - 1}} \right] \tag{4}$$

The values of α_e and α_o are given by the relations -

$$\alpha_o = \frac{3}{4\pi N} \left[\frac{1}{1 + a + \frac{3}{n_o^2 - 1}} \right] \tag{5}$$

where N denotes the number of molecules per c.c. and is written as-

$$N = N_A \frac{\rho}{M} \tag{6}$$

N_A, ρ and M are Avogadro number, density and molecular weight respectively. Thus, knowing the value of α_e and α_o , order parameter (S) can be calculated.

3 Results and Discussion

The variation of principal polarizabilities (α_o / α_e) with temperature for pure samples i.e. Cholesteryl Propionate and Cholesteryl Benzoate is shown in Figure 1 (a) and (b) respectively. The same variation for three homogeneous mixtures is shown in Figure 1 (c), (d) and (e) respectively.

The temperature dependence of the order parameter (S) is calculated using Maier and Saupe’s anisotropic internal field model for pure liquid crystal samples and is shown in Figure 2(a) and (b) respectively and those for mixtures is shown in Figure 2 (c), (d) and (e) respectively.

Table 1 gives the experimental and literature values of transition temperatures for various phases for Cholesteryl Propionate, Cholesteryl Benzoate and their three homogeneous mixtures. Tables 2 and 3 gives the values of order parameter for pure samples and their homogeneous mixtures respectively.

Table 1. Various Transition Temperatures for Pure Samples and Their Mixtures

Materials (Wt. Fraction)		T _{S-ch} [° C]	T _{ch-I} [° C]
Cholesteryl Propionate	Exp. Value	90	94
	Lit. Value	92	96
Cholesteryl Benzoate	Exp. Value	149	175
	Lit. Value	148	176
Mixture - 1 (0.25)	Exp. Value	104	114.5
Mixture - 2 (0.50)	Exp. Value	120	136
Mixture - 2 (0.75)	Exp. Value	133	145

Table 2. Order Parameter for Cholesteryl Propionate and Cholesteryl Benzoate

Cholesteryl Propionate		Cholesteryl Benzoate	
Temperature [°C]	Order Parameter X 10 ²	Temperature [°C]	Order Parameter X 10 ²
81	83.5	145	84.0
83	82.0	149	82.5
85	81.5	153	63.0
84	81.0	157	61.0
89	81.0	161	59.0
91	80.0	163	57.5
93	69.0	167	56.0
95	65.5	171	55.0

Table 3. Order Parameter for Mixture 1, 2 and 3

Mixture - 1		Mixture - 2		Mixture - 3	
Temperature [°C]	Order Parameter X 10 ²	Temperature [°C]	Order Parameter X 10 ²	Temperature [°C]	Order Parameter X 10 ²
100	82.0	113	81.0	127	81.0
101	81.0	115	81.0	129	81.0
103	81.0	117	80.0	131	80.0
105	84.0	119	79.5	133	66.0
107	62.5	121	67.5	135	63.0
109	61.0	123	66.0	137	63.0
111	60.5	125	62.0	139	63.0
113	57.5	127	59.0	141	62.0
		129	57.0	143	60.0
		131	57.0	145	60.0
		133	56.0	147	58.0
				149	56.5
				151	55.0
				153	53.0

3.1 Polarizability

From the graphs, it can be seen that the ratio of principal polarizabilities (α_o / α_e) decreases with increase in temperature for all samples i.e. pure as well as mixtures. This decrease in the ratio of principal polarizabilities with increase in temperature establishes the fact that the degree of order decreases as the temperature increases i.e. less order exists at the higher temperature. At the transition points of solid to cholesteric (S-Ch transition) and cholesteric to isotropic (Ch-I transition) the decrease in the ratio of principal polarizabilities is much sharper. These sharp falls indicate that a phase change has occurred. For the isotropic phase, the ratio of principal polarizabilities (α_o / α_e) is unity. This indicates that in the isotropic phase, the anisotropy of pure

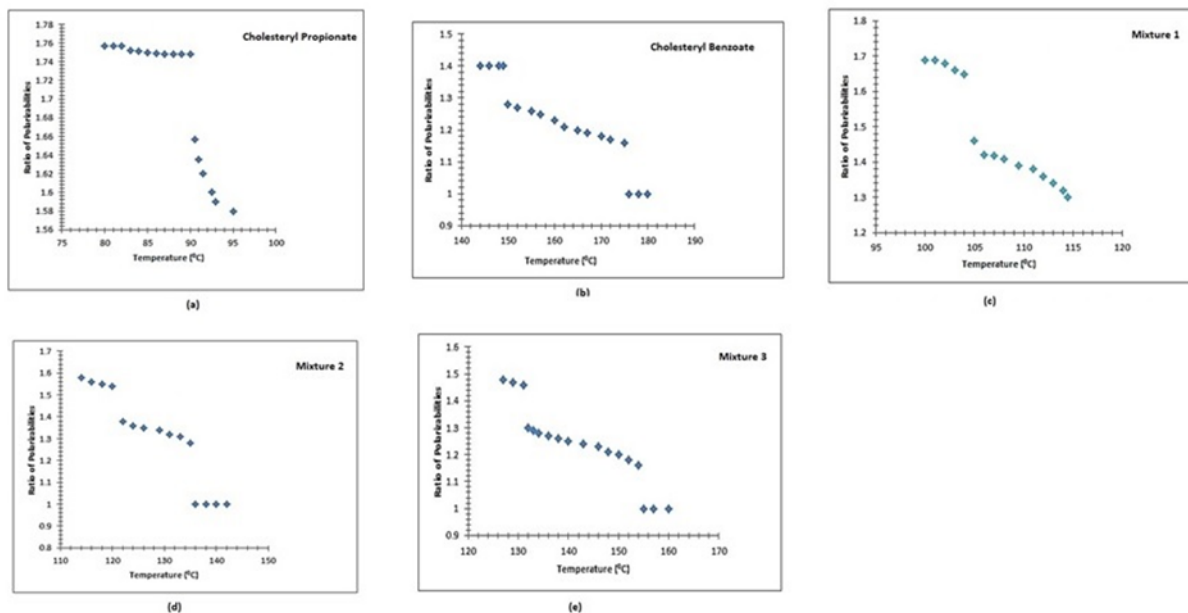


Fig 1. Graph between Temperature (T) and Ratio of Principal Polarizabilities for- (a) Cholesteryl Propionate (b) Cholesteryl Benzoate (c) Mixture 1 (d) Mixture 2 (e)Mixture 3

samples, as well as their mixtures, has vanished. The solid phase shows the higher values of (α_o / α_e) in comparison to the cholesteric and isotropic phase indicating that it is most ordered among the three phases confirming the well-known fact about the solid phase. This also indicates the more rigidity and strongness of the molecular chain in the solid phase.

3.2 Order Parameter

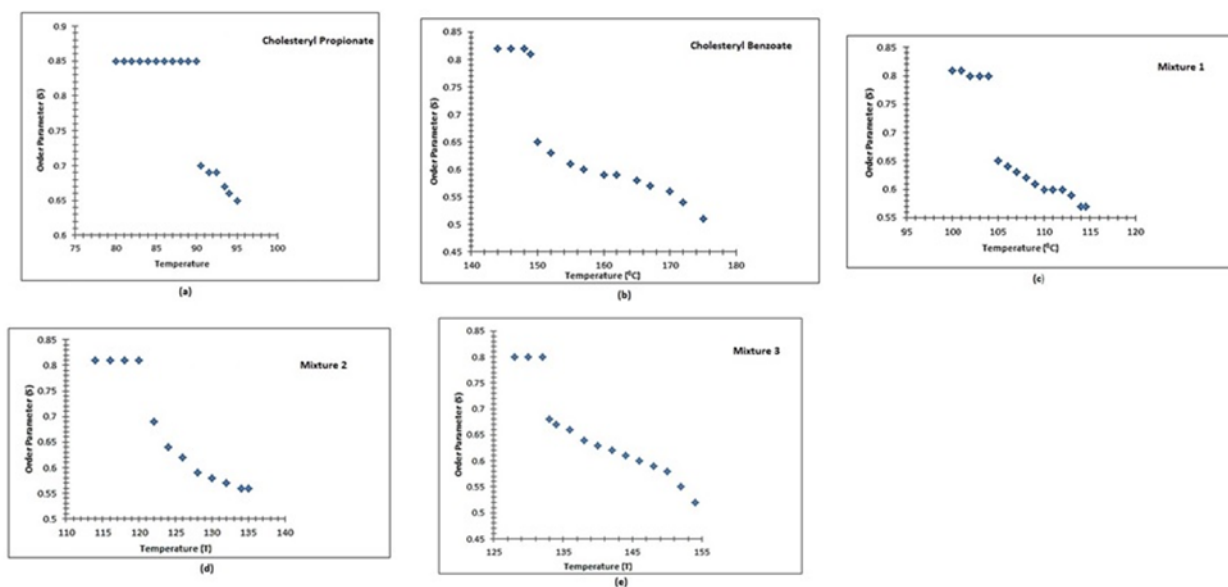


Fig 2. Graph between Temperature (T) and Order Parameter (S) for- (a) Cholesteryl Propionate (b) Cholesteryl Benzoate (c) Mixture 1 (d) Mixture 2 (e)Mixture 3

From the graphs it can be seen that for pure samples as well as for their mixtures (Figure 2 (a) – (e)), the fairly constant behavior of order parameter (S) confirms the definite order in solid phase. The sharp decrease occurs in the order parameter with rise in temperature for the transition from a solid phase to the cholesteric phase (S-Ch transition). This suggests that the liquid crystalline phase is less ordered as compared to the solid phase as expected. After the S-Ch transition, the order parameter (S) goes on decreasing with a further increase in temperature until the cholesteric to isotropic transition (Ch-I transition) occurs. After the Ch-I transition, S becomes zero, establishing the fact of complete randomness of the isotropic phase i.e. no order exists. It is also evident that in the cholesteric phase, the order parameter is more sensitively dependent on temperature.

Earlier studies were performed by some researches on those samples for which the liquid crystalline state was existing in a normal temperature range⁽¹⁸⁾. Also, In recent studies, the materials taken for investigation have their liquid crystalline state either in lower temperature range^{(10), (19)} or in moderate temperature range⁽²⁰⁾ but the present study shows that the maintenance of the liquid crystalline state is not only possible even on higher temperatures (90^oC - 94^oC for Cholesteryl Propionate and 149^oC - 175^oC for Cholesteryl Benzoate) but its tuning is also achievable (104^oC - 145^oC for Mixture 1 to Mixture 3).

4 Conclusion

The present study shows that it is possible to tune the transition temperature of CLCs by mixing them in different concentrations as we have achieved transition temperature for solid to cholesteric phase, 104^oC for Mixture 1, 120^oC for Mixture 2 and 133^oC for Mixture 3. Similarly, the transition temperatures are tuned from 114.5^oC for Mixture 1, 136^oC for Mixture 2 and 145^oC for Mixture 3 for cholesteric to isotropic phase transition. All these transition temperatures for mixtures lies within the range of transition temperatures of pure samples. Further, the abrupt change in the values of optical anisotropy, polarizability and order parameter at the transition temperature also confirms the different phases occurring in CLC samples. The fall in the degree of orderedness from a solid phase to isotropic liquid phase via mesogenic phase with rise in temperature is well indicated by the data. The close agreement of theoretical and experimental values for pure sample establishes the validity of the data obtained. The advantage of using Maier and Saupe's approach to calculate the polarizability and order parameter is that this approach is more realistic as it considers the internal field as the anisotropic one, because liquid crystals are also a medium of anisotropic molecular distribution.

The novelty of this study is that it opens the door for preparing the new materials by mixing the two or more materials in different concentrations and altering their phase transition temperatures as per need. This has great significance in the field of material science while preparing new materials with new properties and novel performance.

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