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The Study of Refractive Indices of Liquid Crystal Mixtures

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In the present study the ordinary refractive indices of Nematic liquid crystal (LC), Cholesteric liquid crystal and their mixtures were measured by multiple wavelength refractometer in the visible range with temperature range from 20°C to 80°C. As the wavelength increases, the refractive indices may decrease. As the temperature increases, the refractive index may decrease. The ordinary refractive index decreases or increases depending on the crossover temperature of the Liquid Crystal employed. The wavelength- and the temperature-dependent refractive indices are fundamentally interesting and practically important for optimizing the display performances and other photonic devices employing LCs.

We also tried to investigate factors affecting the temperature gradient of ordinary refractive index (dno/dT).Liquid crystal should exhibit a large temperature gradient refractive index to reduce the required laser intensity for triggering the nonlinear optical effects. The two crucial parameters for achieving large dno/dT are high birefringence and low clearing point. However, these two requirements are often conflicting each other. The temperature at which $dn_o/dT = 0$ *is called the cross-over temperature To. If Tc, the clearing temperature of liquid crystal material is much higher than the room temperature then the cross-over temperature would be relatively high and* $dn_o/dT < 0$ *at room temperature. From all the investigations it is observed that the values of refractive index change with temperature, wavelengths as well as with the mixture. Some of the liquid crystal mixtures show excellent index matching property.*

Keywords Nematic liquid Crystal (NLC); Cholesteric liquid crystal (CLC); Birefringence; ordinary Refractive Index; Abbe refractometer

1. Introduction

Liquid crystals have various display and non-display applications. Thin-Film transistor liquid crystal display (TFT-LCD) has been commonly used in direct-view, e.g., cellular phones, notebook and desktop computers, and televisions, and large screen projection displays [1, 2]. The fundamental light modulation mechanism of a LCD is the electric field-induced molecular reorientation which causes change in the refractive index. The refractive indices of a liquid crystal (LC) are mainly determined as a function of its constituents,[3] wavelength of the incident light [4] and operating temperature [5]. To achieve a full-color display three primary colors (red, green, and blue) are needed. As

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the wavelength increases, the refractive indices decrease. To design the LC panels for projection displays, we need to know the intended operating temperature. As the temperature increases, the extraordinary refractive index may decrease monotonously, but the ordinary refractive index could decrease or increase depending the crossover temperature of the LC employed [6]. In the Nematic liquid crystal the molecules are aligned parallel to the preferred direction called director. The Cholesteric liquid crystals are also called twisted Nematic liquid crystals because there is a twist angle from one layer to other in Nematic planar structure. The thermotropic liquid crystals are thermally induced. When an external electric field is applied to thermotropic Cholesteric liquid crystal, it changes the pitch of the helix, turns the helical axis and converts it to the nematic phase. The electric field causes the director reorientation. When the light enters liquid crystals it travels parallel to the director with a velocity different from the velocity of a light travelling perpendicular to the director. So the liquid crystals are birefringent [7, 8]. When the light enters liquid crystals, it splits in an ordinary ray which moves faster than the extraordinary ray and when the two rays recombine as they exit the sample because of this phase difference, the polarization state changes [7]. Wavelength, temperature, and molecular constituents play key roles in determining the LC refractive indices. We measured ordinary refractive indices of Nematic liquid crystal, Cholesteric liquid crystal and their four mixtures for nine different wavelengths at the temperature interval of 5°C.

2. Theory

The refractive indices of liquid crystals are mainly determined as a function of its constituents, wavelength of the incident light and operating temperature. Here we discuss wavelength and temperature effect.

2.1 Variation of Refractive Index (n) with Wavelength (λ)

The cholesteric liquid crystals consist of thin birefringent layers normal to the optic axis and each one is turned through a small angle with respect to its neighbours. Because of this turn each linear component of the light experiences a change in refractive index while passing from one layer to the next. The changes will be an increase for the fast and a decrease for the slow component of light [9]. By measuring the refractive index of ordinary ray (no) for the given wavelength of light (λ), pitch (P) of the Cholesteric liquid crystal and the mixtures can be calculated using the relation,

$$\lambda = Pn_0 \tag{1}$$

If d is the spacing between thin birefringent layers of the cholesteric liquid crystals then

$$\lambda = 2dn_0. \tag{2}$$

When light is incident on an atom or molecule, the periodic electric force of the wave sets the bound charges into a vibratory motion having the frequency of the wave. The phase of this motion will depend on the impressed frequency, and will vary with the difference between the impressed frequency and the natural frequency of the bound charges. These induced oscillations of the bound charges generate the secondary waves. The secondary waves traveling in the same direction as the original beam combine to form sets of waves moving parallel to the original waves. According to the principle of superposition of waves the secondary waves must be added to the primary ones. This interference modifies the phase of the primary waves and is equivalent to a change in their wave velocity. So the phase of the oscillators, and hence of the secondary waves, depends on the impressed frequency. This clearly implies that the velocity in the medium varies with the frequency of light [10]. This is the explanation of dispersion that is the variation of the refractive index with the wavelength of light.

The dispersion $\frac{dn}{d\lambda}$ can be calculated from two-constant Cauchy equation,

$$n = A + \frac{B}{\lambda^2} \tag{3}$$

The constants A, B can be obtained by fitting the experimental results at any two wavelengths. From equation 3 the refractive indices and birefringence decrease as the wavelength increases.

Differentiating, dispersion

$$\frac{dn}{d\lambda} = -\frac{2B}{\lambda^3} \tag{4}$$

This shows that dispersion varies approximately as the inverse cube of the wavelength. Dispersion is often measured in terms of the coefficient of dispersion.

$$\text{Coefficient of dispersion} = n_F - n_C \tag{5.1}$$

Another common measure of dispersion is the dispersive power,

$$\text{Dispersive Power} = \frac{n_F - n_C}{n_D - 1} \tag{5.2}$$

The dispersion is also measured by a standard parameter known as Abbe's number or V number.

In equation 5.1 and 5.2 nF, nC and nD are the refractive indices at the wavelengths of the spectral lines 589.3 nm, 486.1 nm and 656.3 nm respectively.

2.2 Variation of Refractive Index (n) with Temperature (T)

Liquid crystals are birefringent and birefringence Δ n is defined as the difference between the extraordinary RI and ordinary RI [4, 11].

$$\Delta n = n_e - n_o \tag{6}$$

The average refractive index <n> is

$$< n > = \frac{n_e + 2n_o}{3} \tag{7}$$

From equations 6 and 7,

$$n_e = \; < n > + \frac{2}{3}\Delta n \tag{8}$$

$$n_o = \; < n > - \frac{1}{3}\Delta n \tag{9}$$

To describe the temperature dependent birefringence, Haller approximation has been commonly employed, [12]

$$\Delta n(T) = (\Delta n)_o \left(1 - \frac{T}{T_C}\right)^{\beta} \tag{10}$$

In equation 10, (Δn)o is the birefringence in the crystalline state, the exponent β is a material constant and TC is the clearing temperature of the liquid crystal material under investigation. The average RI decreases linearly with increasing temperature as

$$< n > = A - BT \tag{11}$$

From equations 9, 10 and 11 we can write

$$n_e(T) = A - BT + \frac{2}{3}(\Delta n)_o \left(1 - \frac{T}{T_C}\right)^{\beta} \tag{12}$$

$$n_o(T) = A - BT + \frac{1}{3}(\Delta n)_o \left(1 - \frac{T}{T_C}\right)^{\beta} \tag{13}$$

Taking temperature derivatives of ne(T) and no(T), from equations 12 and 13 we get

$$\frac{dn_e}{dT} = -B - \left[\frac{2\beta(\Delta n)_o}{3T_C\left(1 - \frac{T}{T_C}\right)^{1-\beta}}\right] \tag{14}$$

$$\frac{dn_o}{dT} = -B + \left[\frac{\beta(\Delta n)_o}{3T_C\left(1 - \frac{T}{T_C}\right)^{1-\beta}}\right] \tag{15}$$

In equation 14 both the terms in the right side are negative and are independent of temperature. This indicates that ne decreases as the temperature increases through the entire nematic range.

However equation 15 consists of negative term (−B) and the positive term which depends on the temperature. There exists a temperature called crossover temperature To for no where $\frac{dn_o}{dT} = 0$.

3. Chemicals and Measurement of Refractive Index

The present study we used Nematic liquid crystal, Cholesteric liquid crystal and their mixtures in four different proportions/concentrations. (Both the samples were procured from ALDRICH)

Sample A: Name of the sample: Cholesteryl Oleate (Nematic phase)

Molecular formula: C45H78O2; Melting point: 48°C.

Sample B: Name of the sample: Cholesteryl Chloride (Cholesteric phase)

Molecular formula: C27H45Cl1; Melting point: 96°C.

Mixtures of the samples were prepared in the different proportions.
5A + 5B: 50% of sample A and 50% of sample B.

4A + 6B: 40% of sample A and 60% of sample B.
3A + 7B: 30% of sample A and 70% of sample B.
2A + 8B: 20% of sample A and 80% of sample B.

The two samples were first weighed accurately using analytical microbalance in the required proportions. Then the mixture was stirred enough to ensure thorough and complete mixing. We measured the ordinary refractive indices of Nematic liquid crystal, Cholesteric liquid crystal and their mixtures with increasing concentration of Cholesteric liquid crystal in the mixtures. The refractive indices for ordinary ray were measured in the visible spectral region using a multiwavelength Abbe Refractometer (DSR-λ by SCHMIDT + HAENSCH) for wavelengths 404.7, 435.8, 486.1, 546.1, 587.6, 589.3, 635.8, 656.3, 706.5 in nm. The accuracy of the Abbe Refractometer is up to fifth decimal. For a given wavelength, we measured ordinary refractive indices of A, B, 5A + 5B, 4A + 6B, 3A + 7B, 2A + 8B from 20°C to 80°C with the intervals of 5°C.

4. Results and Discussions

The measurements of ordinary refractive indices for 3A + 7B are shown in Table 1. Similar measurements are done for A,B,5A + 5B,4A + 6B,3A + 7B,2 + 8B. The sample A which is Nematic liquid crystal measures the refractive indices for selective wavelengths and for limited range of temperatures. Whereas sample B, the Cholesteric liquid crystal measures the refractive indices for all wavelengths and at all temperatures. Similarly the mixtures 5A + 5B, 4A + 6B, 3A + 7B, 2A + 8B also measure the refractive indices for all the wavelengths and at all temperatures.

Figures 1 and 2 show the graphs of refractive index versus temperature for various wavelengths for A, 4A + 6B respectively.

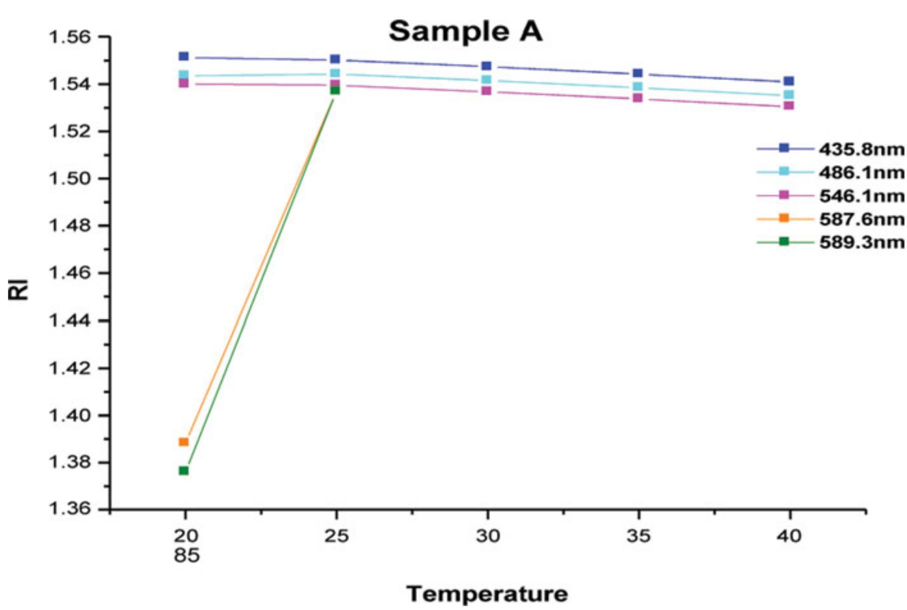

Figure 1. RI vs. Temperature for A.

Table 1. Measurement of ordinary RI for 3A + 7B

WL→(nm) Temp↓(°C)	404.7 RI↓	435.8 RI↓	486.1 RI↓	546.1 RI↓	587.6 RI↓	589.3 RI↓	632.8 RI↓	656.3 RI↓	706.5 RI↓
20	1.53017	1.52458	1.51732	1.51126	1.50826	1.50815	1.50562	1.50444	1.50263
25	1.53172	1.52606	1.51847	1.51209	1.50876	1.50863	1.50577	1.50451	1.50261
30	1.53534	1.52957	1.52176	1.5149	1.51102	1.51087	1.5075	1.50608	1.504
35	1.54064	1.53517	1.52779	1.52106	1.5169	1.51673	1.51288	1.51123	1.50874
40	1.54323	1.53804	1.53147	1.52579	1.52248	1.52236	1.5195	1.51832	1.51616
45	1.53671	1.53147	1.52524	1.51974	1.51686	1.51676	1.5144	1.51327	1.51072
50	1.5245	1.51979	1.51418	1.5095	1.50704	1.50695	1.50484	1.50386	1.50215
55	1.51946	1.51494	1.50961	1.50521	1.50291	1.50283	1.50089	1.5	1.49841
60	1.51796	1.51343	1.5081	1.50372	1.50142	1.50133	1.4994	1.49853	1.49692
65	1.51652	1.51202	1.50671	1.50233	1.50005	1.49997	1.49806	1.49718	1.49557
70	1.51501	1.51052	1.50526	1.50093	1.49867	1.49858	1.49668	1.49581	1.49421
75	1.51339	1.50894	1.50371	1.4994	1.49717	1.49709	1.4952	1.49433	1.49273
80	1.51147	1.50701	1.5018	1.4975	1.49526	1.49518	1.49331	1.49245	1.49085

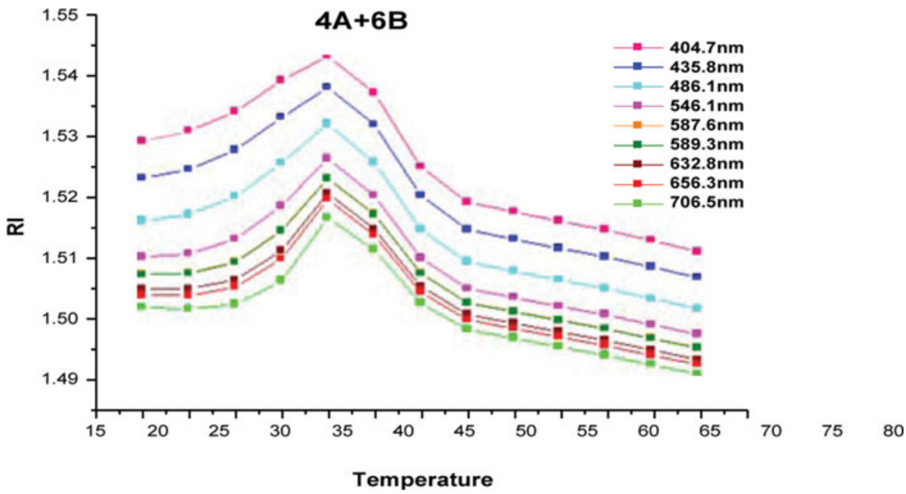

Figure 2. RI vs. Temperature for 4A+6B.

As the temperature increases the density of mass of the isotropic organics decrease which in turn causes the RI to decrease linearly. The graphs for all the mixtures indicate the similar pattern as shown in Fig. 2, the values of RI increase reach maximum value and then decrease.

Figure 3 and 4 show the graphs of refractive index vs wavelengths at different temperatures.

The graphs indicate that the refractive index decreases with increase in wavelength. All the mixtures have a reasonable good index match with Cholesteryl Chloride.

The values of minimum refractive index and maximum refractive index for all the samples are listed in Table 2.

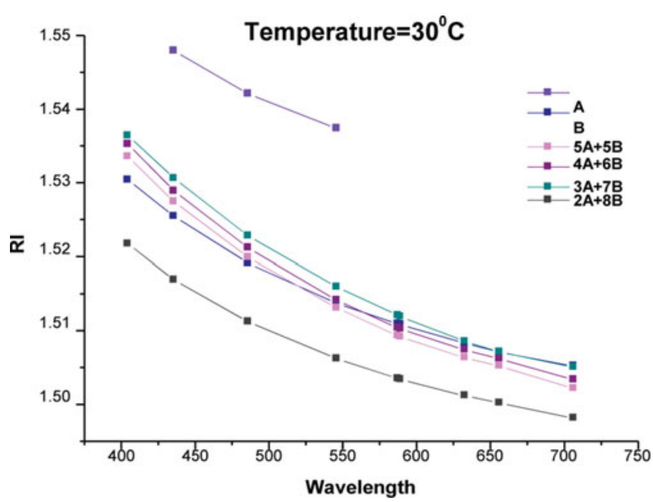

Figure 3. RI vs. Wavelengths at 30° C.

Table 2. Maximum RI and Minimum RI forA, B, 5A + 5B, 4A + 6B, 3A + 7B, 2A + 8B

	Sample A	Sample B	5A + 5B	4A + 6B	3A + 7B	2A + 8B
Maximum RI	1.55978	1.53074	1.53454	1.5435	1.5433	1.52813
Minimum RI	1.37682	1.49066	1.48815	1.4907	1.4908	1.49027
Difference in RI	0.18296	0.04008	0.04639	0.0537	0.052	0.03786

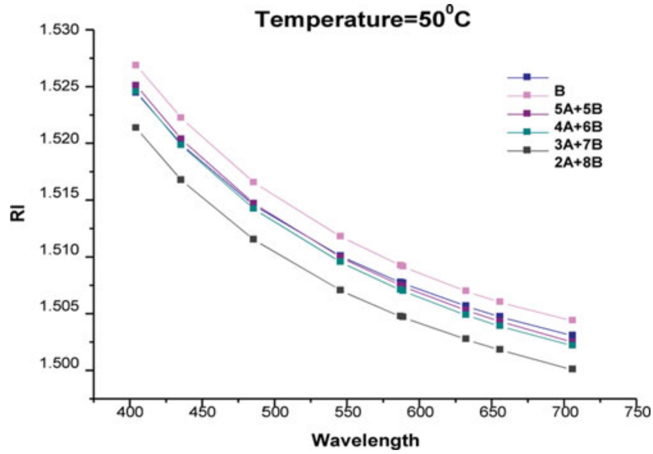

Figure 4. RI vs. Wavelengths at 50° C.

The graph of maximum RI vs wavelength for 5A + 5B, 4A + 6B, 3A + 7B and 2A + 8B is as shown in the Fig. 5. Figure 6 shows the temperature at which the individual mixture has maximum value of RI.

The mixtures 4A + 6B and 3A + 7B show maximum refractive indices at 40°C. The mixtures 5A + 5B and 2A + 8B show maximum refractive index for temperature 45°C.

The trends seen in the refractive index behavior can be related to the microscopic structural changes that occur in the composites which strongly affects the molecular orientational degree of freedom. Thus each molecule undergoes a structural rearrangement and attains a lower energy state.

The effect of wavelength on the distance between the successive layers at 30°C is presented in Table 3.

Table 3 shows the calculated values of the pitch and the distance between the successive layers for nine different wavelengths at 300°C for samples B, 5A + 5B, 4A + 6B, 3A +

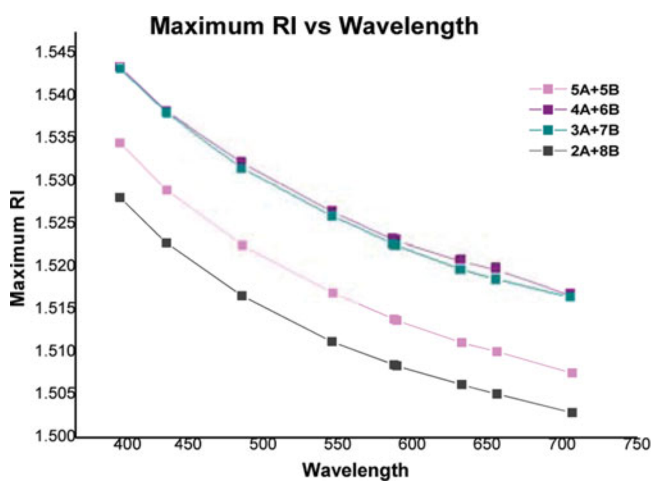

Figure 5. Maximum RI vs. Wavelength for different samples.

Table 3. Pitch and the distance between the successive layers of B, 5A + 5B, 4A + 6B, 3A + 7B, 2A + 8B

λ nm →	404.7	435.8	486.1	546.1	587.6	589.3	632.8	656.3	706.5
B									
P nm	264.626	285.883	320.209	361.017	389.17	390.324	419.832	435.776	469.704
d nm	132.31	142.942	160.105	180.509	194.59	195.162	209.916	217.888	234.852
5A + 5B									
P nm	264.075	285.512	320.045	361.168	389.588	390.749	420.387	436.323	470.652
d nm	132.038	142.756	160.023	180.584	194.794	195.375	210.194	218.162	235.326
4A + 6B									
P nm	263.789	285.239	319.775	360.917	389.314	390.474	390.474	436.036	470.276
d nm	131.895	142.62	160.388	180.459	194.657	195.237	210.047	218.018	235.138
3A + 7B									
P nm	263.589	284.917	319.433	360.486	388.876	390.04	419.768	435.767	469.747
d nm	131.795	142.459	160.217	180.243	194.438	195.02	204.384	217.884	234.824
2A + 8B									
P nm	266.133	287.497	321.886	362.821	391.097	392.255	421.83	437.787	471.919
d nm	133.067	143.749	160.943	181.411	195.549	196.128	210.92	218.894	235.960

no = refractive index of ordinary ray, p = pitch and λ = wavelength of the light used.

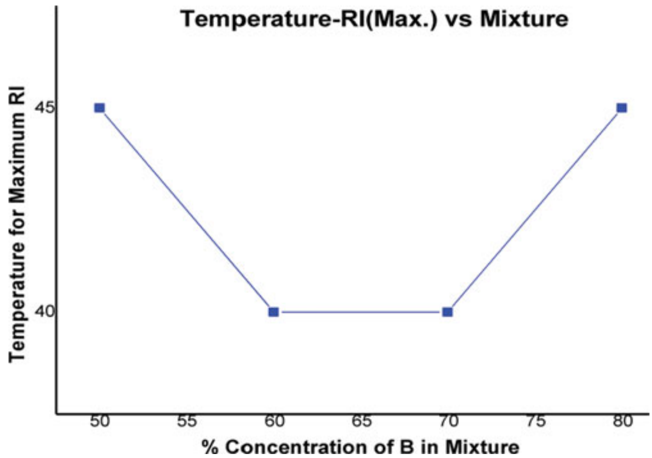

Figure 6. Temperature for maximum RI vs. Mixture.

7B,2A + 8B using equation 1 and equation 2. The calculated values of pitch for all the mixtures match with the pitch of cholesteric liquid crystal (sample B) in the mixtures. For all the wavelengths, the value of pitch is minimum for the sample 3A + 7B. Similarly the distance between the two successive layers of the sample 3A + 7B is minimum amongst all the values.

The Table 4 indicates the values of fitting constants A, B, dispersion, coefficient of dispersion, dispersive power and Abbe number at 30°C for mixtures 5A + 5B, 4A + 6B, 3A + 7B, 2A + 8B using equations 3, 4, 5.1, 5.2 and 5.3.The dependence of RI on wavelengths

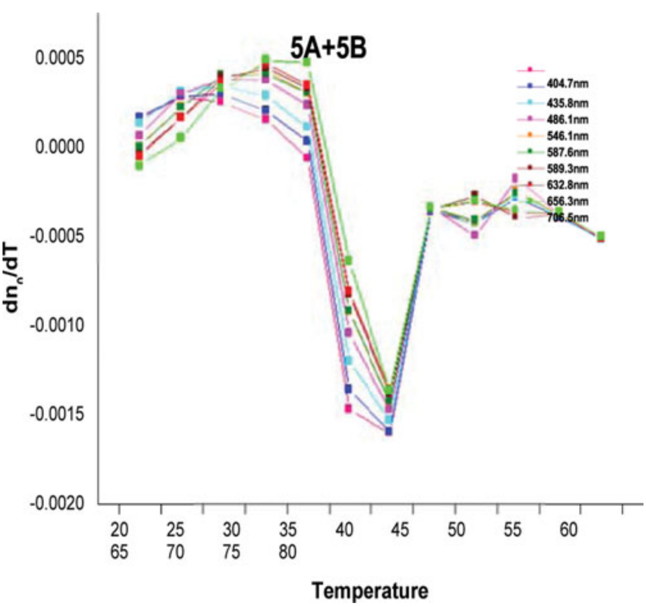

Figure 7. Temperature derivative of ordinary RI vs. Temperature for 5A + 5B.

Table 4. Dispersion in relation to RI for 5A + 5B, 4A + 6B, 3A + 7B, 2A + 8B

	5A + 5B	4A + 6B	3A + 7B	2A + 8B
Fitting constant A	1.4853	1.48589	1.48767	1.48569
Fitting constant B	0.0079263$\mu m2$	0.0080889$\mu m2$	0.008052$\mu m2$	0.005782$\mu m2$
Dispersion	−0.0046215	−0.0047064	−0.0046693	−0.0034104
Coeff. of dispersion	0.01469	0.01498	0.01568	0.01103
Dispersive power	0.0289099	0.0294193	0.0306927	0.0219584
Abbe number	34.590197	33.991322	32.580995	45.54064

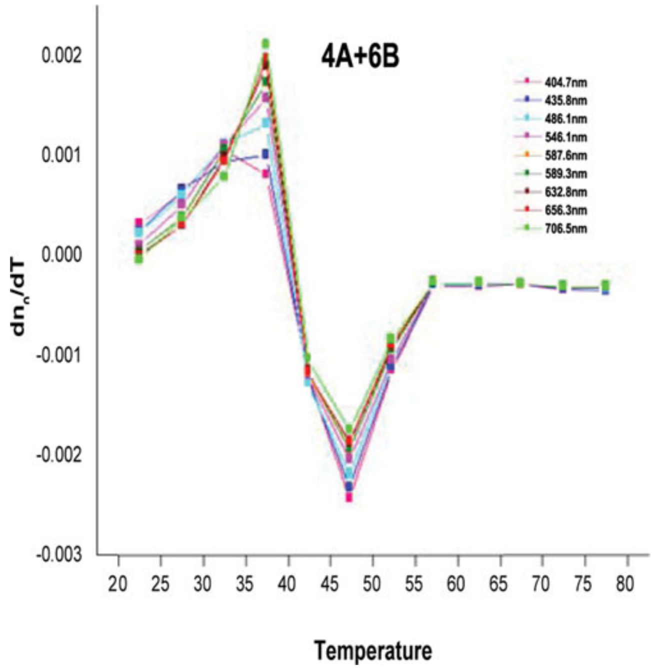

Figure 8. Temperature derivative of ordinary RI vs. Temperature for 4A + 6B.

varies with the concentration of Cholesteryl Chloride in the mixtures. Maximum dispersion occurs for 70% concentration of cholesteric liquid crystal in the mixture. The molecules of 3A + 7B among all the mixtures emit maximum number of secondary waves in phase with the incident light wave causing maximum dispersion.

The phase transition temperatures of all four mixtures were measured by using differential scanning calorimetry technique at 2°C/min scanning rate.

The relation between refractive index and temperature at different wavelengths for the mixtures of the thermo- tropic liquid crystals was studied and interpreted by considering that the kinetic energy of the molecules increases and their orientations change with increase of temperature, and due to this change the optical path of the light inside the molecule increases.

The values of β, $(\Delta n)_o$, $\frac{dn_o}{dT}$ for all the mixtures were calculated using equations 13 and 15.The calculated values contradicted with the values obtained by previous researchers [6, 11]. Since we have data only of ordinary refractive indices we could not calculate A and B using equation 11.

So we calculated temperature derivative of ordinary refractive index $\left(\frac{dn_o}{dT}\right)$ from the measured values of the ordinary refractive index for all the mixtures. The graph of $\frac{dn_o}{dT}\,vs.$ temperature was plotted for all the mixtures and the temperature at which $\frac{dn_o}{dT}$ is zero was determined by graph. This is the cross-over temperature TO. The graphs of temperature derivative of ordinary refractive index vs. temperature for 5A + 5B and 4A + 6B are shown in Figs. 7 and 8 respectively.

Table 6 presents the cross-over temperature and the values of (dno/dT) max. Since many devices prefer to operate at room temperature, (dno/dT) max for temperature ranges 25°C −30°C and 30°C −35°C are given in Table 6. The cross-over temperature changes

Table 5. Clearing temperature T_C (°C) for 5A + 5B, 4A + 6B, 3A + 7B, 2A + 8B

Mixture	Clearing Temperature T_C (°C)
5A + 5B	95.35
4A + 6B	93.07
3A + 7B	91.83
2A + 8B	96.77

Table 6. Cross-over temperature TO (°C) and the maximum value of temperature derivative of RI (dno/dT) max in per °C for 5A + 5B, 4A + 6B, 3A + 7B, 2A + 8B

		Temperature range in °C	
Mixture	Cross-over Temp To°C	25–30 (dn_o/dT)max	30–35 (dn_o/dT)max
5A + 5B	43.7	0.000278	0.000404
4A + 6B	40.5	0.000634	0.001108
3A + 7B	40	0.000724	0.001232
2A + 8B	44.75	0.00069	0.000446

with the concentration of Cholesteryl Chloride in the mixture. It is minimum for3A + 7B. The (dno/dT) is maximum for the mixture 3A + 7B in both the ranges and it is∼3X higher than 5A + 5B as well as 2A + 8B in the range 30°C −35°C.

5. Conclusions

In this paper, our main aim is to determine the effect of the molecular structure, wavelength, and operating temperature on the refractive indices for ordinary ray of a liquid crystal. It has been observed that the refractive indices for ordinary ray of the mixtures are different than the individual constituents. The pattern of the graphs for mixtures indicates that hindrances in the path of light through the mixtures, are unaffected by the proportion of individual constituents in the mixtures. The refractive indices for the ordinary ray decrease with the increase in wavelength. All the LC mixtures have good RI match with Cholesteryl Chloride. It implies that the RI match is not the only factor affecting the concentration but LC miscibility also plays important role.

We also observed that the mixture having 70% concentration of Cholesteryl Chloride offers maximum value of temperature gradient of RI in the temperature range 25°C −35°C (around room temperature) and it is ∼3X higher than other two mixtures.

From all the investigations it is observed that the values of refractive index change with temperature, wavelengths as well as with the mixture. Some of the liquid crystal mixtures have shown excellent index matching property.

These properties of liquid crystal mixtures we studied hold promise in various display and non-display applications.

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