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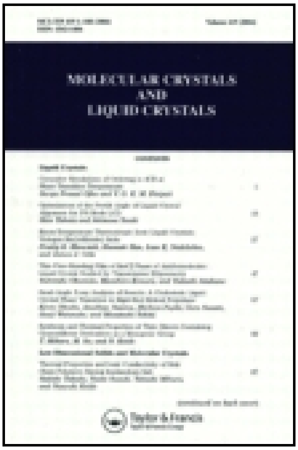

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# Optical Behavior and Related Properties of the Binary Mixture 5CB/8CB Liquid Crystals

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# Optical Behavior and Related Properties of the Binary Mixture 5CB/8CB Liquid Crystals

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*The index of refraction in the isotropic phase,* n, *and in the mesophase,* $n_o$, *for pure 5CB and 8CB liquid crystals, as well as their binary mixtures, were measured as a function of temperature. The related parameters, namely the orientational order parameter (*S*), relative polarizability anisotropy (*$\zeta$*), and molecular length-to-breadth ratio (*k*), were calculated and compared for the mesophase of the considered samples. The order parameter and the relative polarizability anisotropy had maximum values for the binary mixture that had a eutectic composition. The low values observed for the (k), either for pure or mixed states, suggest the arrangement of parallel molecules within the nematic phase persists in group "swarms."*

**Keywords:** binary mixtures; index of refraction; liquid crystals; polarizability

## 1. INTRODUCTION

Liquid crystal is a state of matter that is neither a solid crystal nor an isotropic liquid. Liquid crystals exhibit anisotropy in their mechanical, electrical, and optical properties, behaving in this sense as solid crystal. Nevertheless, they have no ability to support shearing, and thus they flow like ordinary liquids [1]. This is why liquid crystals attain their importance in technological applications, especially in electro-optic switches and in liquid-crystal displays [2]. Therefore, thermal stability of liquid-crystalline mesophase and its molecular ordering are of great importance.

It was suggested [3] that the determining factor for a compound to form a liquid-crystalline mesophase is the tendency for its molecules to adhere to one another sideways. This lateral adhesion is dependent on

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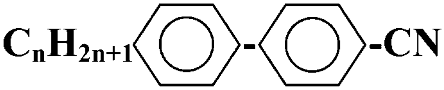
the molecular shape and the extent of dipole–dipole attractions. Lateral projections from rod-shaped molecules decrease the stability of the mesophase, presumably by geometrical interference with the necessary parallel orientation. It was also suggested [3] that the p-phenylene groups might favor lateral attractions in molecules containing them. This is caused partly by enhanced van der Waals attractions, due to the presence of the polarizable $\pi$-electrons, and partly by enhanced polarity, due to conjugation with attached groups. The 4-alkyl-4′-cyano biphenyl compounds **I** satisfy these criteria.



**( I )**

The two different alkyl-substituted derivatives of **I**, namely 4-n-pentyl (5CB) and 4-n-octyl (8CB) derivatives, were thoroughly investigated in the literature [2] in their pure state, but little information concerning their binary mixtures are given. The present work aims to investigate the optical behavior and related properties of the 5CB/8CB binary mixture throughout the whole composition range.

## 2. EXPERIMENTAL

### 2.1. Materials

The two homologous liquid crystals 5CB and 8CB (Merck) were used without further purification. Their purity was checked through the detection of their transition temperatures using differential scanning calorimetry (DSC) and polarized light microscopy. Their values agreed well with those reported in the literature [4].

### 2.2. Preparation of the Mixtures

Binary mixtures of 5CB/8CB that cover the whole range of composition were prepared by mixing the individual components at 45°C, a temperature that is sufficient to transform them to their isotropic phase. Mixtures of the two components in known proportions were prepared at that temperature by weighing the appropriate amounts of both components, mixing, and then cooling in air to room temperature.

### 2.3. Refractive Index Measurements

Measurements of the refractive index, in the temperature range of 20 to $50 \pm 0.2$°C, were performed using an Abbe 60 refractometer

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attached to an ultrathermostat. Refractive index measurements at temperatures other than 20°C were corrected to compensate for the change of refractive index of the prism brought about by the working temperature, because the instrument had been initially calibrated for 20°C. The correction amounts to 0.0000078 per 1°C.

## 2.4. Calorimetric Measurements

Calorimetric investigations were performed with a differential scanning calorimeter (PL-DSC, England) with nitrogen as a purge gas. The instrument was calibrated from the melting points of ultrapure metals, and a value of 28.45 J/g was used for the enthalpy of fusion of indium. The typical heating rate was 10 K/min, and sample masses were 2–3 mg. Data were used to construct the phase diagram for the binary mixture of 5CB/8CB. From the phase diagram, a eutectic composition of 31.38 mol% 8CB was determined.

# 3. RESULTS AND DISCUSSION

The measured refractive index in the isotropic phase, n, and in the mesophase, $n_o$, as function of temperature for the pure components (5CB and 8CB), as well as their binary mixtures at different compositions, is presented in Fig. 1. The extraordinary light refractive index, $n_e$, values were out of the range measured by the refractometer. Thus, they were calculated from the relation

$$n^2 = \frac{(n_e^2 + 2n_o^2)}{3} \tag{1}$$

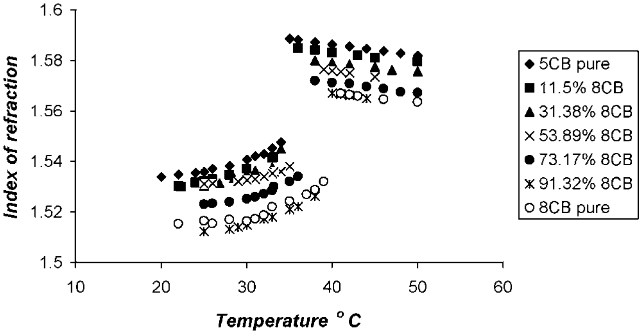

**FIGURE 1** Temperature dependence of the refractive index of pure 5CB and 8CB liquid crystals and their binary mixture.

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The values of $n_o$, n, and $n_e$ were used to calculate the orientational order parameter S, the relative polarizability anisotropy $\zeta = \alpha_\perp/(\alpha_{II} - \alpha_\perp)$, and the molecular length-to-breadth ratio k at different temperatures for all pure and mixed samples.

Different methods are generally used to calculate the order parameter. These are the methods of Neugobauer [5], Saupe and Maier [6], Palffy-Mahoray and Balzarini [7], and Vuks [8]. Vuks' method is based on an isotropic internal field model, whereas the other methods are based on an anisotropic internal field model. However, the S-values calculated by all these methods were found to be not significantly different [9,10].

In the present work, the S-values for the investigated mixtures have been evaluated using the isotropic internal field model of Vuks [8]. In this model, S is given by

$$S = \frac{\alpha}{\alpha_{||} - \alpha_\perp} \times \left[\frac{n_e^2 - n_o^2}{n^2 - 1}\right] \tag{2}$$

where $\alpha$ is the mean polarizability and $\alpha_{||}$ and $\alpha_\perp$ are the principal polarizabilities in directions parallel and perpendicular to the optic axis. To simplify Equation (2), let

$$\delta = \frac{1}{3}\left(\frac{\alpha_{||} - \alpha_\perp}{\alpha}\right). \tag{3}$$

By multiplying Equation (2) by Equation (3), one gets

$$\delta S = \frac{1}{3}\left(\frac{n_e^2 - n_o^2}{n^2 - 1}\right). \tag{4}$$

Using the refractive index data, $\delta S$ could be calculated. To get $\delta$, the Haller *et al.* method [11] of extrapolating to a zero temperature a linear fit to the plots $\ln(\delta S)$ and $\ln(1 - T/T_c)$ was used. The intersection at zero temperature, that is at $S = 1$, gave the $\delta$-value. The order parameter S could, thus, be evaluated for various samples at different temperatures, and the results are tabulated in Table 1.

## 3.1. Variation of Order Parameter with Composition and Temperature

Figure 2 shows the variation of S with temperature for pure components and their eutectic binary mixture (31.38 mol% 8CB). In the figure, this composition was only presented to avoid graph crowding and to directly compare with the previously reported data. It is obvious from the figure that the S-value at the eutectic composition is larger than either of the two pure components. The same behavior of the

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**TABLE 1** Order Parameter for All Various Mixture Compositions Calculated at Different Temperature within the Nematic Phase

| T (°C) | 100% 5CB | 11.50 mol% 8CB | 31.38 mol% 8CB | 53.89 mol% 8CB | 73.17 mol% 8CB | 91.32 mol% 8CB | 100% 8CB |
|---|---|---|---|---|---|---|---|
| 39 | | | | | | | 0.4161 |
| 38 | | | | | | 0.4334 | 0.4593 |
| 37 | | | | | | 0.4643 | 0.4847 |
| 36 | | | | | 0.4057 | 0.478 | 0.5046 |
| 35 | | | | | 0.4296 | 0.4886 | 0.525 |
| 34 | | | | 0.5582 | 0.454 | 0.5057 | 0.5504 |
| 33 | 0.4766 | 0.38 | 0.7687 | 0.5779 | 0.472 | 0.5243 | 0.5592 |
| 32 | 0.499 | 0.3925 | 0.778 | 0.5901 | 0.4887 | 0.5324 | 0.6018 |
| 31 | 0.5137 | 0.4025 | 0.7841 | 0.5985 | 0.5043 | 0.5642 | 0.6234 |
| 30 | 0.5296 | 0.4153 | 0.7918 | 0.6206 | 0.5169 | 0.5883 | 0.6381 |
| 29 | 0.5497 | 0.4305 | 0.8 | 0.6314 | 0.5284 | 0.6 | 0.6388 |
| 28 | 0.5697 | 0.4426 | 0.8075 | 0.6406 | 0.5351 | 0.6127 | 0.6385 |
| 27 | 0.5813 | 0.4525 | 0.8149 | 0.6504 | 0.5448 | 0.6234 | 0.6632 |
| 26 | 0.5929 | 0.4546 | 0.8248 | 0.6562 | 0.5512 | 0.6346 | 0.6586 |
| 25 | 0.6036 | 0.4769 | 0.8299 | 0.6622 | 0.5559 | 0.6476 | 0.6832 |
| 24 | 0.6142 | 0.4891 | 0.8338 | 0.6696 | 0.5586 | 0.6596 | |
| 22 | 0.6314 | 0.5076 | 0.84042 | 0.6762 | 0.5608 | 0.6778 | |
| 20 | 0.6561 | 0.5275 | 0.8446 | 0.6794 | 0.5652 | | |

temperature dependence of S has been reported before for the nematic binary mixtures of (hexoxy/heptoxy) and (pentyl/heptyl) cyanophenyls [10,12], where in both cases the eutectic mixture possesses higher order parameter than either of the pure components. Nevertheless, the previous studies did not consider the variation of S throughout the whole composition range.

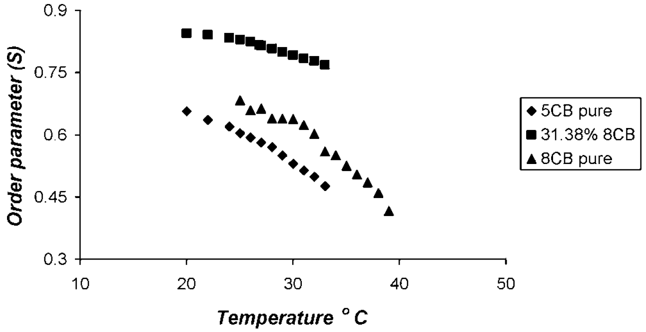

**FIGURE 2** Temperature dependence of the order parameter for pure 5CB and 8CB liquid crystals and their eutectic composition.

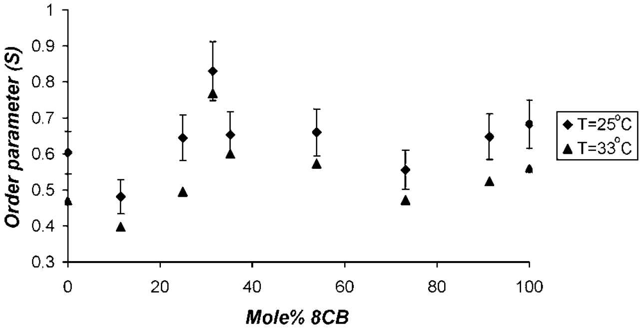

**FIGURE 3** Variation of the order parameter $S$ with the mixture composition at two different temperatures.

Figure 3 represents the composition dependence of S at two different selected temperatures (25 and 33°C) to be within the nematic phase. It is clear from the figure that first, the two curves at the two chosen temperatures behave similarly, except that S-values are larger at lower temperatures, as expected. Second, the mixture at the composition of the eutectic possesses the highest order parameter, within the investigated range of composition.

It was suggested [3] that when a solid crystal melts to form a mesophase, the molecular arrangement within the mesophase is greatly influenced by the crystalline structure of the solid. As a result, for any composition of a binary mixture, the order parameter of the nematic phase is highly affected by the molecular ordering within the crystalline solid from which it is formed. This ordering will persist within the nematic phase until it vanishes at the clearing temperature. So, the comparison of the order parameter in the nematic phase just before the transition to isotropic phase (i.e., at the clearing temperatures), should have the same trend as that at any other lower temperature within the whole nematic phase. Accordingly, entropy change, $\Delta s_c$, at temperature transition, $T_c$, from nematic to isotropic phase can safely be used to describe this criterion.

## 3.2. Variation of Entropy Change of Various Samples at Different Temperatures

Transition temperatures ($T_c$) and enthalpies ($\Delta H_c$) for the investigated samples, as measured by differential scanning calorimetry (DSC), are collected in Table 2. From these data, $\Delta s_c$ was calculated and plotted in Fig. 4 as a function of mixture composition. It is observed from the figure that at the eutectic composition, $\Delta s_c$ has its minimum value.

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**TABLE 2** Clearing Temperatures ($T_c$, °C) and Enthalpies of Transition from Nematic to Isotropic Phase ($\Delta H_c$, kJ/g) for Pure 5CB and 8CB as well as Their Binary Mixture

| Mol % 8CB | $T_c$ | $\Delta H_c$ |
|---|---|---|
| 0 | 34.97 | 0.281 |
| 11.50 | 35.20 | 0.264 |
| 31.38 | 35.95 | 0.185 |
| 53.89 | 37.08 | 0.236 |
| 73.17 | 38.25 | 0.255 |
| 91.38 | 39.23 | 0.299 |
| 100 | 40.08 | 0.359 |

This minimum $\Delta s_c$ value corresponds to a maximum molecular ordering value for the eutectic composition, which is in accordance with the results obtained for S calculations.

## 3.3. Composition Dependence of Polarizability

The molecular polarizabilities ($\alpha$, $\alpha_{||}$, and $\alpha_{\perp}$) are physical properties of liquid-crystal molecules. Their temperature dependence is usually used to monitor changes in molecular conformation. Polarizability anisotropy ($\alpha_{||} - \alpha_{\perp}$), on the other hand, determines how the physical properties of molecules are changed with changes in their core or in the length of the alkyl chain; a property we are interested in. To exclude the effect of density on the temperature and composition dependences of ($\alpha_{||} - \alpha_{\perp}$), the relative polarizability anisotropy

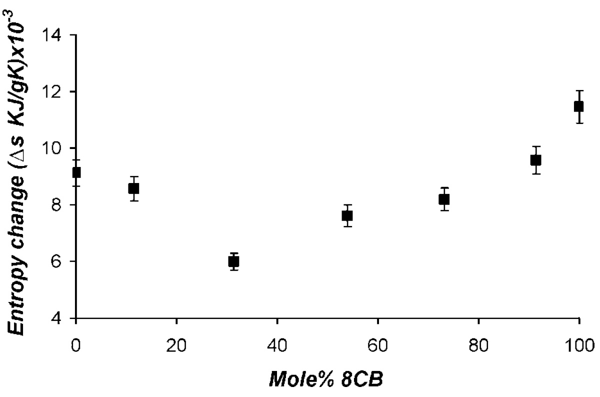

**FIGURE 4** Variation of entropy change with in mixture composition.

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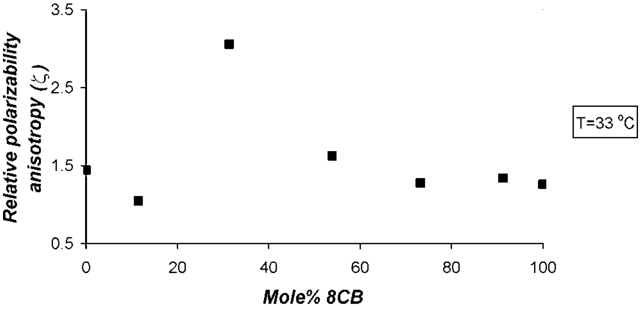

**FIGURE 5** Relative polarizability anisotropy as function of mixture composition.

$\zeta = \alpha_{\perp}/(\alpha_{||} - \alpha_{\perp})$, which is also a measure of the polarizability anisotropy, has been evaluated from the relation [13]

$$\zeta = \frac{\alpha_{\perp}}{(\alpha_{||} - \alpha_{\perp})} = \left[\frac{k_A(n^2 - 1)}{(n_e + n_o)}\right] - \frac{1}{3} \tag{5}$$

where $k_A$ is a coefficient in the Valentova *et al.* equation [14].

In this manner, the relative anisotropy, $\zeta$, was calculated and plotted as function of mixture composition in Fig. 5. It is seen from the figure that $\zeta$ possesses again its maximum value at the eutectic composition, which is in accordance with the obtained results of the order parameter and entropy change. This may clarify that the molecules arrange themselves side by side rather than end to end.

The plot of $\zeta$ versus temperature, Fig. 6, shows a slight linear decrease with increase of temperature. It also shows that $\zeta$ is always

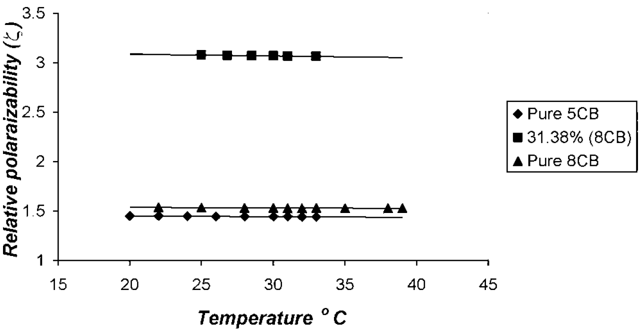

**FIGURE 6** Temperature dependence of the relative polarizability anisotropy for pure 5CB and 8CB liquid crystals and their eutectic composition.

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greater for 8CB than 5CB, because of the increased number of $CH_2$ groups, as has been reported before [13].

### 3.4. Length-to-Breadth Ratio

The molecular hard core length-to-breadth ratio, k, is an important factor when calculated, and when analyzed it may throw more light on how the molecules arrange themselves in the nematic phase. Palffy-Muharay and Balzarini [15] have calculated k for butyl p-(p-ethoxyphenoxycarbonyl) phenyl carbonate from the slope of local field tensor and order parameter. They got $k = 1.25$, which they considered to be a low value for such a molecule. They argued that it is due averging over molecular conformation.

The same treatment has been followed in the present study to calculate k, and the results are plotted as function of mixture compositions in Fig. 7. From the figure it is seen that the values for pure components of 5CB and 8CB are about 1.43 and 1.49, respectively, whereas for the eutectic composition (maximum order parameter) k has its minimum value (1.23). These data suggest that the lower values of k may not be due to changes in the conformation of molecules but much more probably because the molecules arrange themselves in group "swarms" [3]. These swarms form in the solid and persist upon melting to the mesophase. On the mesophase, molecules in each swarm have their own direction, which differs from one swarm to another. In this way, k seems to be an average over all the molecules within the swarm. As the concentration approaches the eutectic composition, the number of molecules per swarm increases, thus leading to a lower value of k.

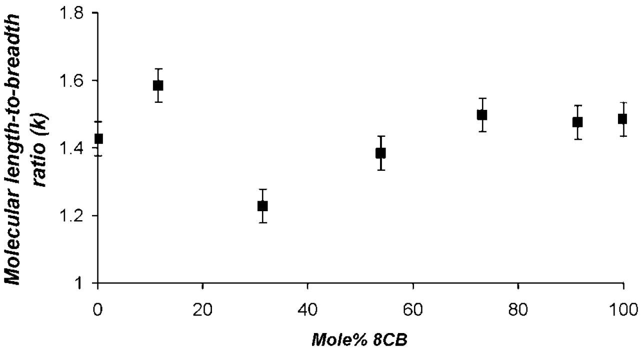

**FIGURE 7** Variation with composition of the molecular length-to-breadth ratio.

## 4. CONCLUSION

From the refractive index data of pure 5CB and 8CB liquid crystals and their binary mixture, the order parameter S, entropy change Δs, relative polarizability anisotropy $\alpha_{\perp}/(\alpha_{||} - \alpha_{\perp})$, and molecular length-to-breadth ratio k were calculated and analyzed. In the nematic phase of the eutectic composition (31.38 mol% 8CB), S has its maximum value, whereas Δs has its minimum value; that is, this phase possesses maximum molecular ordering. The composition dependence of $\alpha_{\perp}/(\alpha_{||} - \alpha_{\perp})$ on the mole percent within the nematic phase showed a parallel trend to that of the order parameter. Both together may suggest that as the eutectic composition is approached, the molecules arrange themselves laterally rather than end to end. The estimated low k-values for the molecules and its observed minimum at the eutectic composition support the swarm formation.

## ACKNOWLEDGMENT

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