3

Chapter 3

3.1 Electro Optic and Elastic Constant Measurements on Some Mixtures of Compounds Made of Rod-like and Bent-core Molecules

As we described in Chapter 1, liquid crystalline phases are exhibited by organic compounds whose molecules have shape anisotropy. Compounds with molecules having two different shapes, viz, rod-like (R) and disc-like (D) have been studied in great detail in the past [1, 2]. The recently discovered liquid crystals (LCs) made of banana-shaped or bent-core (BC) molecules are being presently studied extensively [9, 33]. Most of the mesogenic rod-like molecules usually have an aromatic core and aliphatic chains attached to one or both ends of the core. A typical BC molecule

has an aromatic bent-core (with a large bend angle of $\sim 120\,^\circ$) made of several phenyl rings connected together using some linkage groups. In most of the compounds, aliphatic chains are attached to both ends of the aromatic core. Unlike R and D molecules, the BC molecules have *shape polarity*. Most of the BC compounds show a variety of novel (B-type) liquid crystalline phases that are unique. A few BC compounds also exhibit the nematic phase [34]. The B-type phases have either 1-dimensionally periodic lamellar or 2-dimensionally periodic columnar structures. Liquid crystals with layered structures formed of R and BC molecules have different symmetries and they are immiscible. Recently [13, 14] detailed studies have been carried out on mixtures of two binary systems of compounds having R and BC molecules by carefully matching the chemical nature and the physical dimensions of the two types of molecules. The temperature-concentration phase diagrams of the two binary systems with the same BC compound 1,3-phenylene bis[4-(3-methylbenzoyloxy)] 4′-*n*- dodecylbiphenyl 4′ -carboxylate (BC12) [35] (Figure 3.1a) and two different rod-like compounds, viz. 4–biphenylyl 4″-*n*-undecyloxybenzoate (BO11) [13], (system I) and 4-*n*-octyloxy 4′-cyanobiphenyl (8OCB) [14] (system II) (Figure 3.1b) have been established. In this chapter, our interest is to study various physical properties exhibited by such mixtures in the *nematic* phase. System II has been used for the experimental studies reported in this chapter as it exhibits wide nematic ranges (see the concentration-temperature phase diagram in Figure 3.2). The 8OCB molecules have the strongly polar cyano end groups and neighbouring polar molecules have an antiparallel orientation and overlap at the aromatic cores [36] giving rise to the partial bilayer SmA_d phase. System II exhibits three induced phases, viz. the biaxial smectic-A (SmA_{db}) phase and two types of 2-dimensionally periodic phases B_1' and B_1 in appropriate concentration ranges of BC12. We are interested in the concentration ranges with ≤ 25 Mol% of BC12.

In this chapter we describe detailed measurements of the following physical properties in the nematic phase of a few different compositions **:** optical birefringence, parallel and perpendicular dielectric constants, and the splay and bend elastic constants, all of which have been measured using a *single* sample mounted in an appropriate cell.

There have been earlier measurements by Dodge *et al.* [37, 38] of the bend elastic constant K_{33} in mixtures of 8OCB with a different compound with BC molecules (1,3-phenylene bis[4-(4heptyl phenyliminomethyl) benzoate] known as P-7PIMB). The mixtures had a relatively low concentration of BC molecules and exhibit nematic and uniaxial SmA phases. The bend elastic
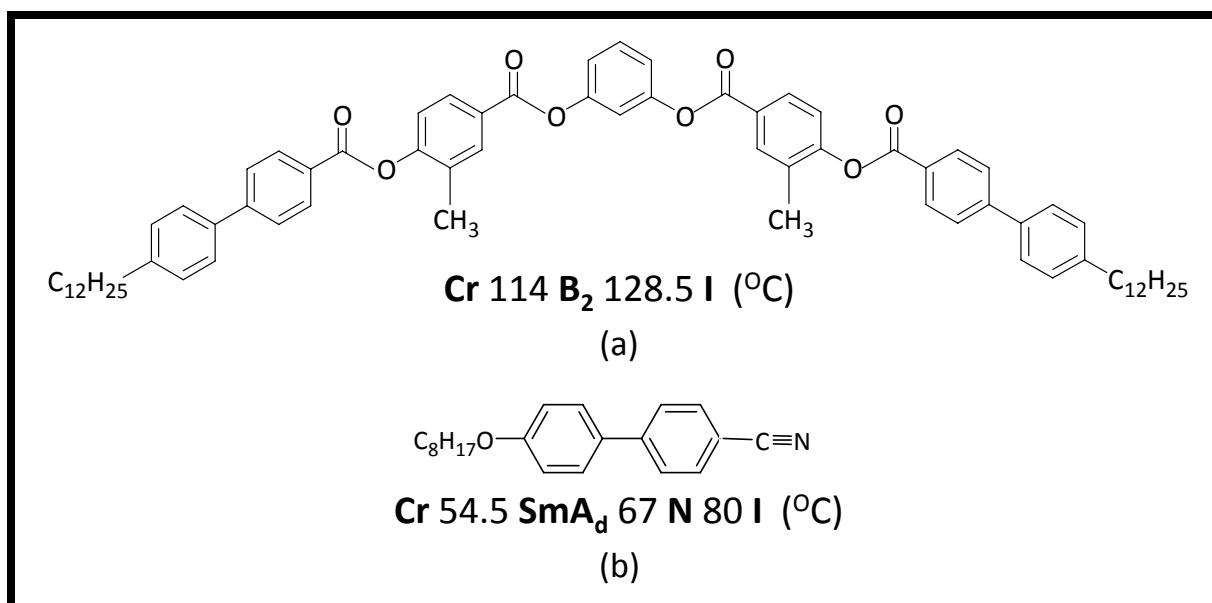
FIGURE 3.1: Molecular structures and phase sequences exhibited by (a) 1,3-phenylene bis[4-(3-methylbenzoyloxy)]4'-*n*- dodecylbiphenyl 4' -carboxylate (BC12) and (b) 4-*n*-octyloxy 4'-cyanobiphenyl (8OCB). Temperatures are in °C.

constant was found to decrease [38] by ∼40% by adding only 3 Mol% of the bent-core compound at 10°C below the nematic-isotropic transition temperature and well above the smectic-nematic transition temperature (see Figure 3.3).

The mixtures used in our study have comparatively larger concentrations of the BC molecules, and exhibit the N, SmA_d and induced biaxial SmA_{db} phases. The mutual orientation of the R and BC molecules in the SmA_{db} phase has been established by other studies[14, 39]. It has been shown that the aromatic cores and aliphatic chains of BC12 molecules fit into the partial bilayer of 8OCB molecules as shown in Figure 3.4, with the arrow axes of the bent-core molecules preferentially lying parallel to the layer normal. The attractive dispersion interaction energy varies as $-\alpha_1\alpha_2 r^{-6}$, where α_1, α_2 are polarizabilities and r is the distance between the interacting parts of the molecules. The interaction energy shows a steep variation with r, and the polarizability of the aromatic part of the molecule is much larger compared to that of the aliphatic part. In the mixtures exhibiting the SmA_{db} phase, it can be expected that this interaction favours the aromatic parts of the R and BC molecules to be close together as shown in Figure 3.4.

In the R rich mixtures of System II, the nematic phase is exhibited over large temperature ranges
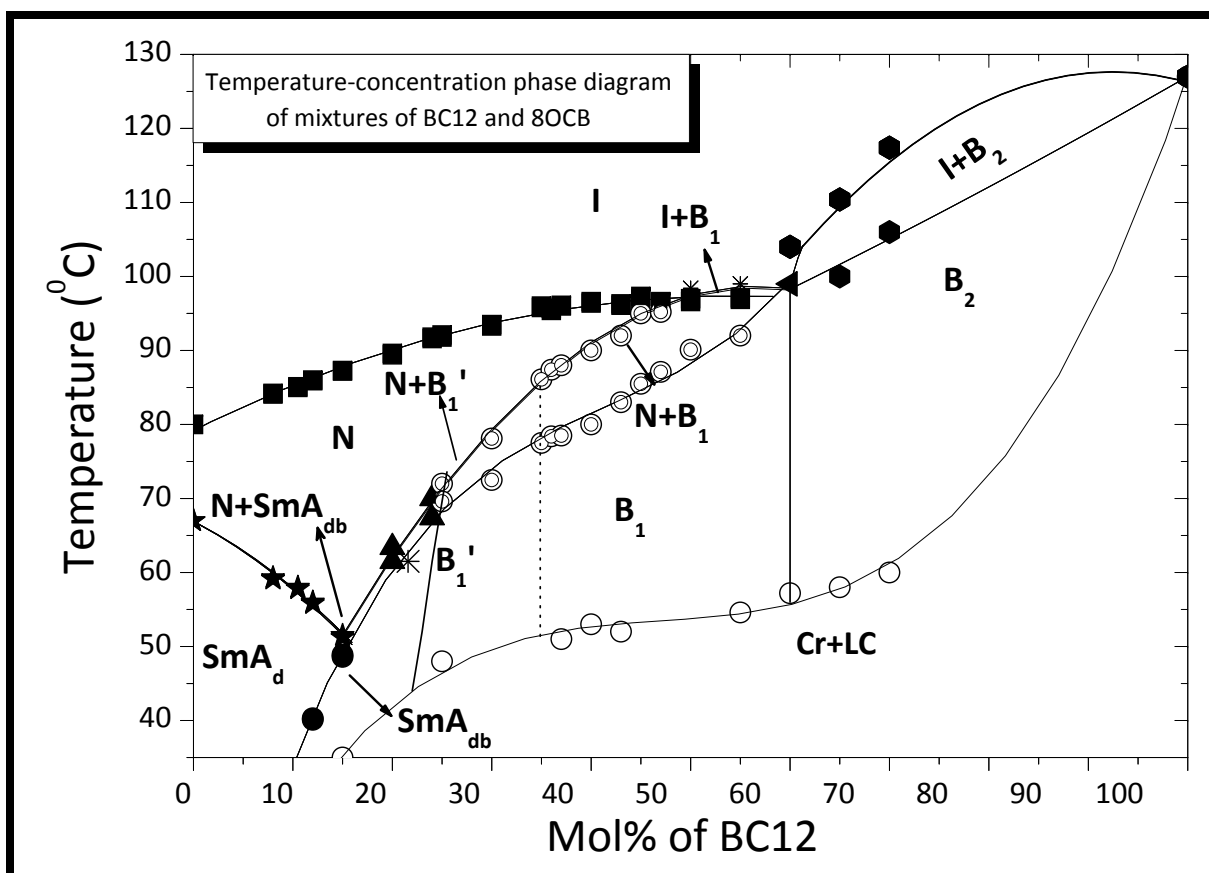
FIGURE 3.2: Temperature-concentration phase diagram of the binary mixture (system II, reproduced from Ref. [14])

and the mutual alignment of the two types of molecules can change with temperature, affecting various physical properties. We have undertaken the present work to explore this possibility.

3.2 Experimental Procedure

BC12 was synthesized and purified in our chemistry laboratory [35] and 8OCB was obtained from Hoffmann-La Roche. Each component of a given mixture was weighed in appropriate quantities in a small glass bottle, which was heated upto $10°$C above the clearing point. Further, the contents were physically mixed by stirring with a glass rod and maintained at that temperature for 10 minutes, before filling the sample into the experimental cell.

We have already discussed about construction of cells in the 2nd chapter, in Section 2.2. In the
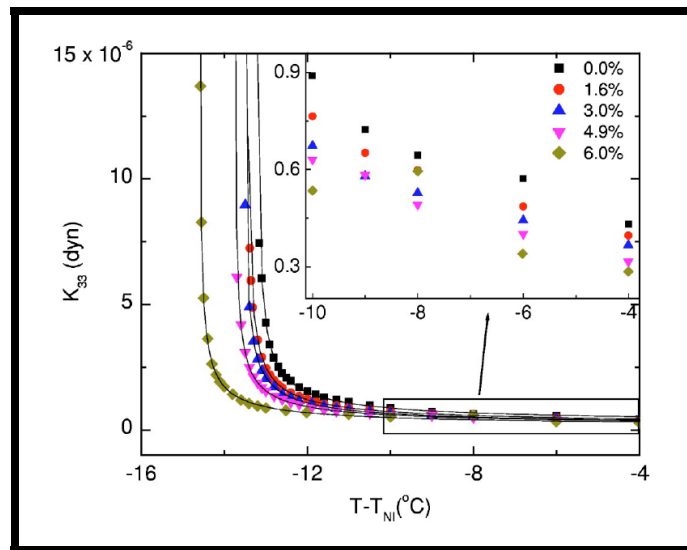
FIGURE 3.3: Bend elastic constant vs relative temperature for different mixtures made of 8OCB and P-7PIMB. Adopted from Ref. [38])
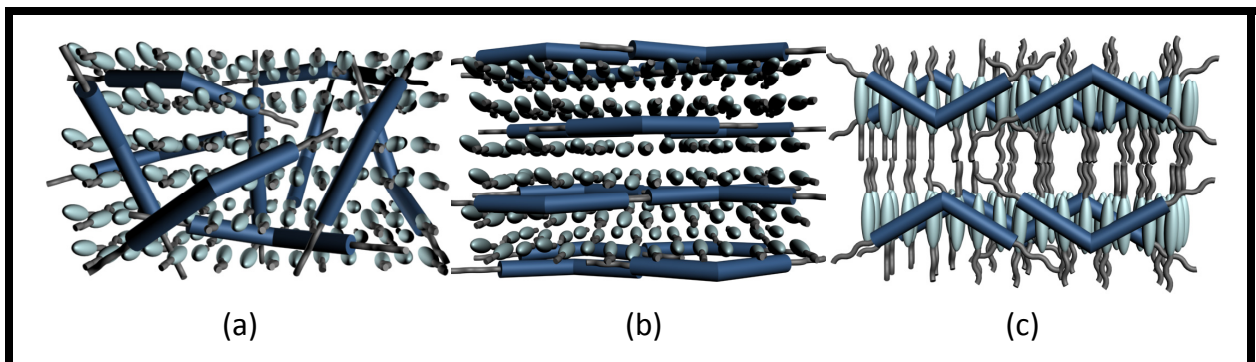

FIGURE 3.4: Schematic representation of the molecular arrangement in the smectic liquid crystal of the mixtures. Top view of a layer of (a) uniaxial smectic (SmA_d), (b) biaxial smectic (SmA_{db}) and side view of (c) SmA_{db} liquid crystal.

experiments on the mixtures, we have used SiO coated planar type cells enclosed in a pill-box. The electro optical setup has been described in Section 2.4 to measure the optical birefringence, both parallel and perpendicular dielectric constants, and the splay and bend elastic constants.
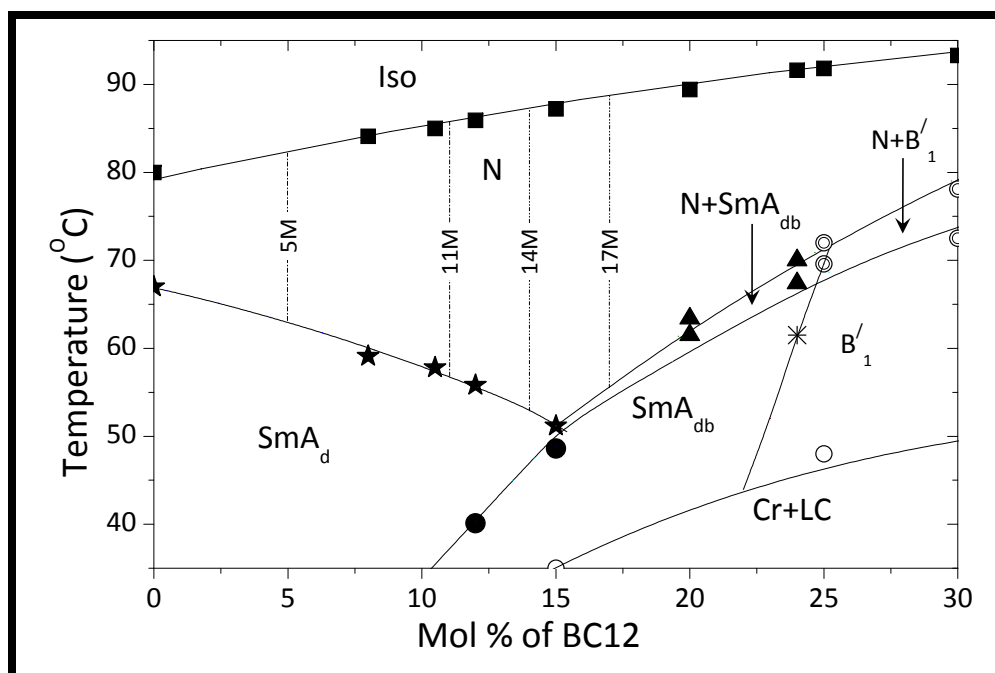
FIGURE 3.5: Expanded temperature-concentration phase diagram of the binary mixture (system II, reproduced from Ref. [14]). The vertical dashed lines correspond to the mixtures on which physical measurements have been made.

3.3 Experimental Results and Discussions

We have studied 8OCB and its mixtures with 5, 11, 14 and 17 Mol% of BC12. In all further discussions these mixtures are denoted as 5M, 11M, 14M and 17M respectively, and indicated by vertical dashed lines in the expanded phase diagram shown in Figure 3.5.

3.3.1 Birefringence and Orientational Order Parameters :

The birefringence data of various mixtures are shown in Figure 3.6. We note the following points.

(i) The birefringence (Δn) of pure 8OCB and all the mixtures increase with decreasing temperature, the variation being quite sharp near the nematic to smectic transition point.

(ii) At any given relative temperature ($T_{NI} - T$), Δn decreases with increasing concentration of the BC compound. This trend is a consequence of the lower anisotropy of polarizability ($\Delta \alpha = \alpha_\zeta - \frac{\alpha_\xi - \alpha_\eta}{2}$) of the BC molecule as compared to that of 8OCB molecule. The

subscripts refer to the principal molecular axes of the BC molecule, which will be defined in Chapter 4 (see Figures 4.1 and 4.13).

(iii) In 5M and 11M mixtures Δn increases slowly as the temperature is lowered in the SmA$_d$ region, while in the 14M mixture (in which the smectic range is relatively large Figure 3.5), there is a shallow minimum.
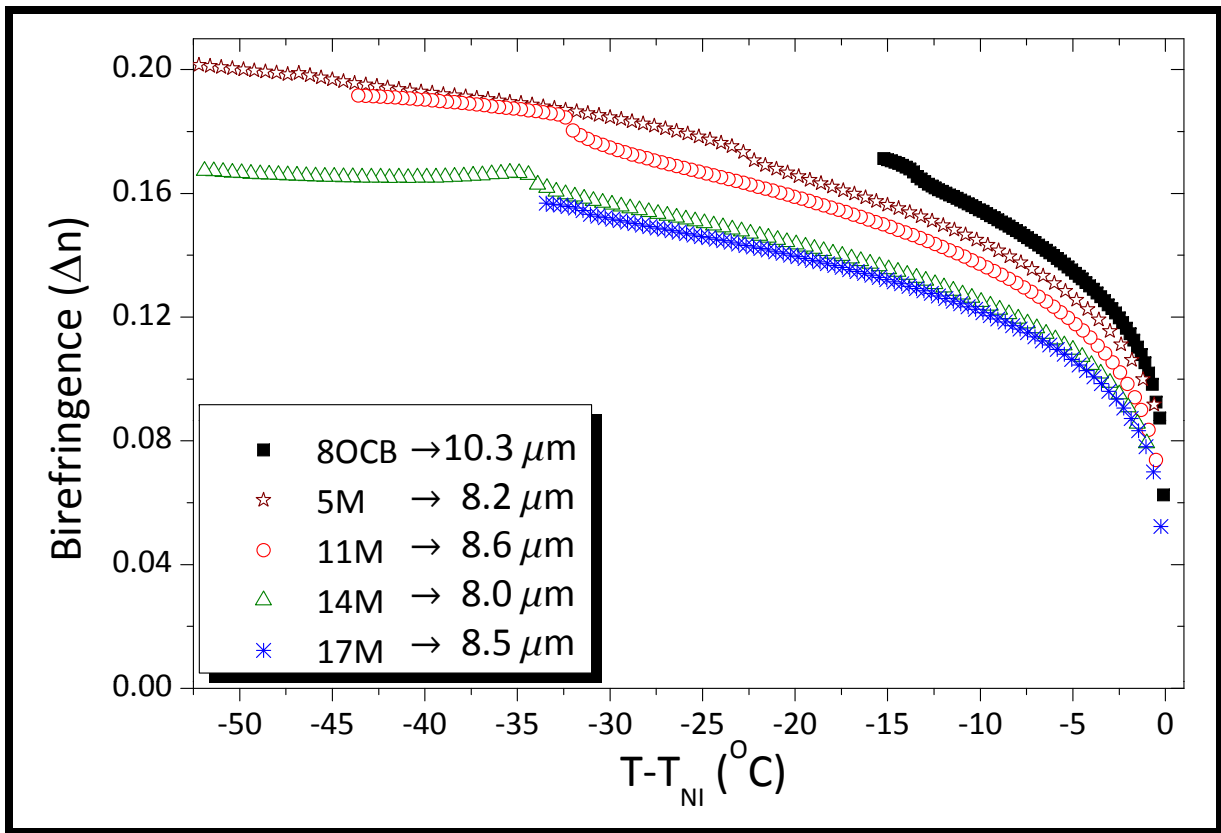

FIGURE 3.6: Dependences of birefringence of pure 8OCB and four mixtures on the relative temperatures. Thickness of the cells are also shown in the inset.

In the mixtures studied the nematic director is defined by the rod-like 8OCB molecules. The SiO coating aligns the director defined by the long axes of the rods. The orientational order parameter of the two types of the molecules should be different in the uniaxial nematic phase. This aspect will be discussed later in Chapter 4. We can however get a gross idea of the macroscopic order parameter of the medium using the birefringence data, by following Haller's procedure[40]. In this, the temperature variation of the birefringence data

is extrapolated to O°K. If the birefringence takes the value Δn_0 (at O°K) for the sample with complete order,

$$\Delta n = \Delta n_0 \left(1 - \frac{T}{T^{**}} \right)^{\beta} \tag{3.1}$$

where Δn_0, T^{**} which is slightly above T_{NI} and β are adjustable parameters. The ratio $\Delta n / (\Delta n_0)$ is a measure of the order parameter (S). The birefringence Δn of pure 8OCB and the four mixtures are fitted by Equation (3.1). The birefringence data of 8OCB and all the mixtures are fitted in the range $-8°C \leq (T - T_{NI}) \leq 0°C$ and $-12°C \leq (T - T_{NI}) \leq 0°C$ respectively. The fit parameters Δn_0, T^{**} and β are shown in Table 3.1. T_{NI} and T^{**} steadily increase with increase of BC concentration and T^{**} is only slightly higher than T_{NI} in each case. The index β is smallest for pure 8OCB and for mixtures it is very close to 0.2. This is much smaller than the mean field value of 0.5. This reduced value of β is also found for a large number of other nematogens made of only rod-like molecules[1]. The reduction in β may be caused by the contribution of the strong fluctuations of the director[1]. The birefringence Δn_0 initially increases for 5M mixture, and for higher concentrations of the BC molecules, Δn_0 steadily decreases. The BC molecules are highly biaxial in shape. The order parameter of such a molecule can not be described by a single number even in the uniaxial nematic phase. We will describe this aspect in the next chapter. And as the concentration BC molecules increases the influence of the molecular biaxiality order parameter should become stronger. The initial increase and later monotonic decrease of Δn_0 probably has a contribution from this tendency.

(iv) The calculated order parameters are plotted in Figure 3.7. Though the differences in the order parameters of the mixtures are not too large, they exhibit a non-monotonic behaviour with the concentration of BC molecules.

3.3.2 Dielectric Constants and Dielectric Anisotropy :

The dielectric constants of all the samples were measured at a frequency of 5.64kHz.

Sample	T_{NI}(°K)	T^{**}(°K)	β	Δn_0
8OCB	354.5	354.6	0.17	0.28
5M BC12	357.1	357.6	0.21	0.30
11M BC12	360.0	360.1	0.21	0.29
14M BC12	361.6	361.7	0.19	0.25
17M BC12	362.3	362.4	0.19	0.24

Table 3.1: Estimated values of T^{**}, the exponent β and Δn_0 for 8OCB and four mixtures. These are the fit parameters of Haller's extrapolation formula.

(i) In all the mixtures the dielectric constant (ϵ_{iso}) in the isotropic phase is lower than that of pure 8OCB. The strong dipole moment of 8OCB molecule enhances the ϵ_{iso} value of that compound. The dielectric constants ϵ_{iso} vary non-monotonically with the concentration of BC12.

(ii) As the sample is cooled the dielectric constant perpendicular to the director ($\epsilon_\perp$) sharply drops in the nematic phase from that in the isotropic phase and the dielectric constant parallel to the director ($\epsilon_\parallel$) increases in the nematic phase from isotropic phase for pure 8OCB and all the mixtures(see Figure 3.8 and 3.9). This shows that, all the mixtures have *positive dielectric anisotropy* mainly due to the high concentration of 8OCB molecules. As the temperature is lowered, $\epsilon_\perp$ continuously decreases reflecting increase of order parameter(see Equation (1.18) of Chapter 1). In the nematic phase at any given relative temperature the variation of $\epsilon_\perp$ is non-monotonic with the concentration of BC12. The ordering of BC molecules should be described by two order parameters. As in the case of birefringence, the contributions from dipole moment and polarizability to the dielectric constant should involve both the order parameters.

(iii) There is a further decrease of $\epsilon_\perp$ at the nematic to smectic phase transition temperature T_{AN}. In the mixtures, the decrease near T_{AN} increases with concentration of BC12, which arises both from enhanced order parameter in the smectic phase[1], and also a change in the mutual orientation of the molecules as will be discussed later.
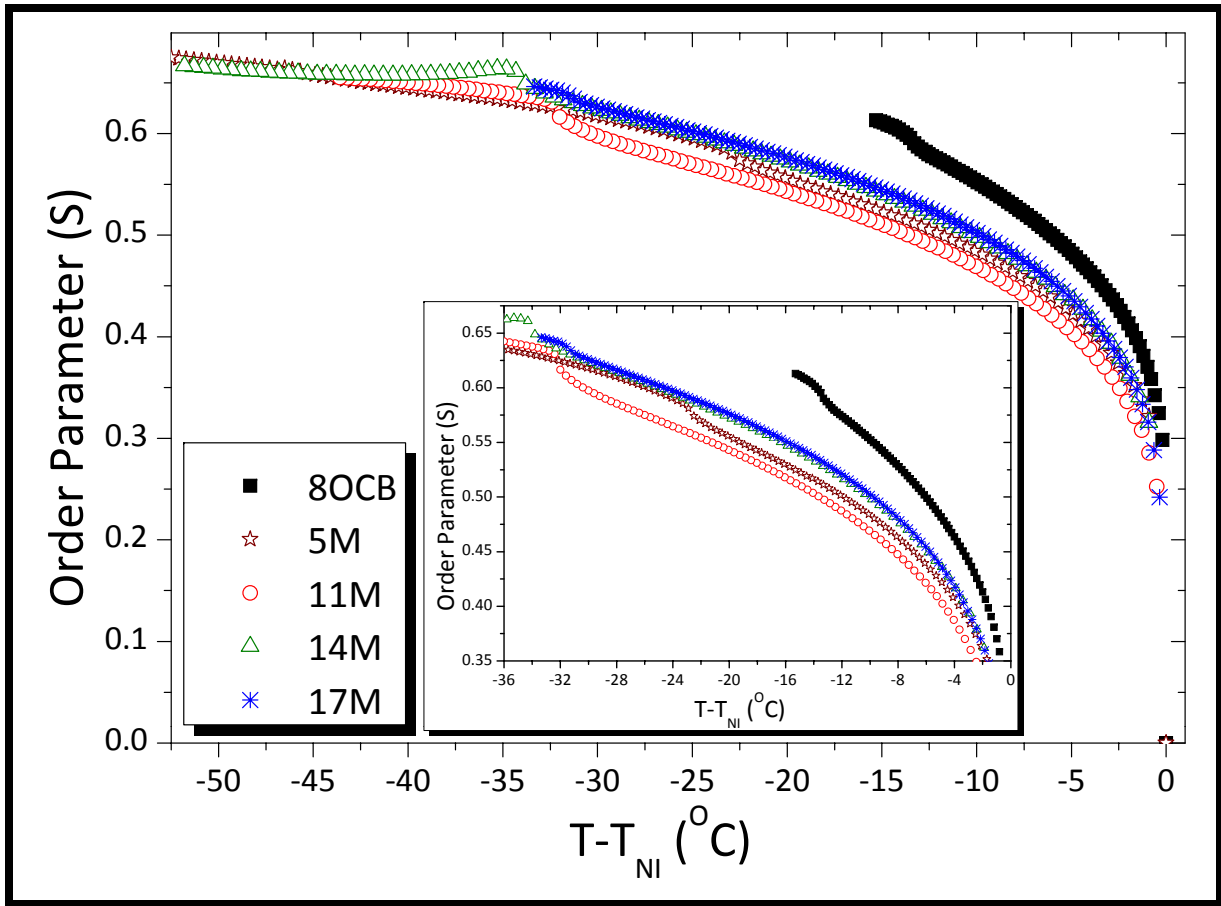
FIGURE 3.7: Dependences of order parameter of pure 8OCB and four mixtures on the relative temperatures. The scale of the y-axis is enlarged in the inset.

$\epsilon_\parallel$ has been measured by extrapolating the high voltage data to $1/V = 0$. As such $\epsilon_\parallel$ is measured only in the N phase in most cases. A detailed description of the method is given in Section 2.7 of Chapter 2.

(iv) At any given relative temperature $\epsilon_\parallel$ decreases with increase in the concentration of BC12 (see Figure 3.9). As in the case of $\epsilon_\perp$ this is a consequence of the lowered concentration of the highly polar 8OCB molecules.

(v) The parallel dielectric constant $\epsilon_\parallel$ of 8OCB monotonically increases up to SmA$_d$. In 5M, $\epsilon_\parallel$ saturates at lower temperatures of the N phase (Figure 3.9). In 11M, 14M and 17M mixtures, as the nematic to SmA$_d$ transition point is approached *within about* 3°C of the transition, $\epsilon_\parallel$ *decreases sharply*(see Figure 3.9). In the above cases the parallel dielectric
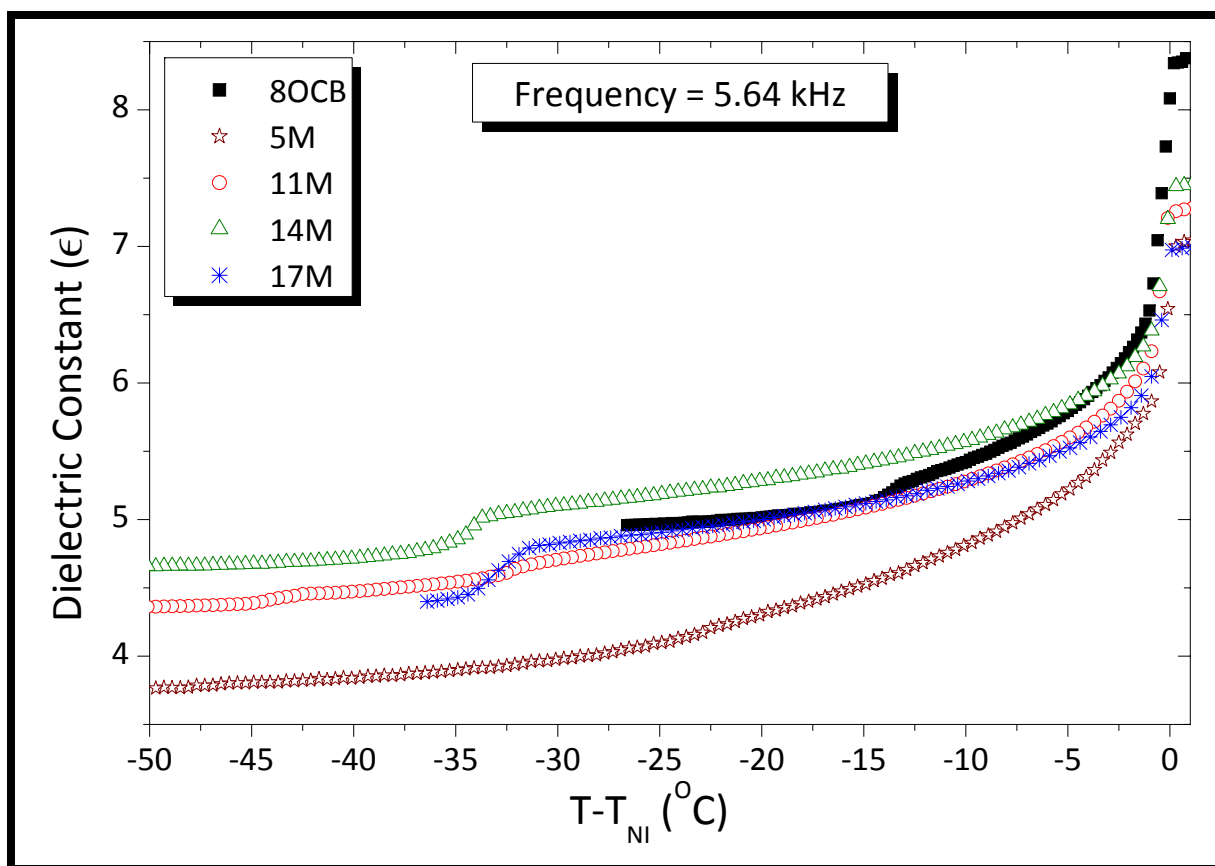
FIGURE 3.8: Dependences of $\epsilon_\perp$ of pure 8OCB and four mixtures on the relative temperatures.

constant $\epsilon_\parallel$ was measured by extrapolation to infinite voltage using homogeneously aligned samples (see Section 2.7 of Chapter 2).

To check if the sharp variation of $\epsilon_\parallel$ near T_{AN} is genuine, $\epsilon_\parallel$ was directly measured using a homeotropically aligned sample in a 22M mixture (thickness = 8.4 μm) using a very small voltage (0.5V). The measurement of $\epsilon_\parallel$ can now be made in both N and SmA_{db} phases (Figure 3.9). $\epsilon_\parallel$ is found to drop sharply from the N phase to SmA_{db} phase, as in the other mixtures. This sharp decrease results from the smectic like short range order which builds up close to the transition point. The alignment of BC molecules in such short range ordered groups should be like that shown in Figure 3.4(a) with their arrow axes along the director defined by the long axes of 8OCB molecules. The contribution of the BC molecules to the dielectric constant is sharply reduced. This reduction implies that there is a large
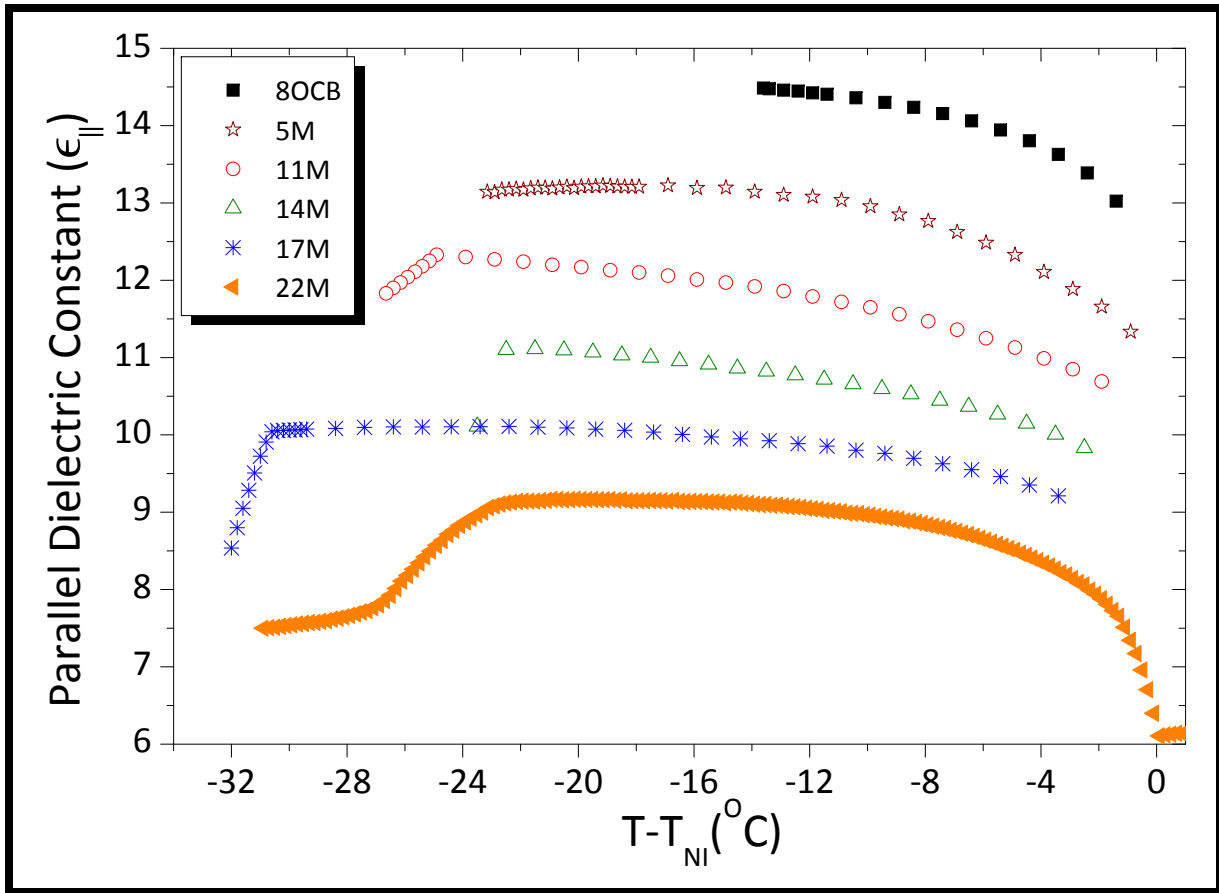
FIGURE 3.9: Dependences of $\epsilon_\parallel$ of pure 8OCB and five mixtures on the relative temperatures. $\epsilon_\parallel$ of 22M mixture is measured using a homeotropically aligned cell.

barrier against the reorientation of the BC molecules about the bow axis in the smectic layers. This is seen in the 22M mixture where we can measure $\epsilon_\parallel$ in the smectic phase(see Figure 3.9). This observation also implies that the *BC and 8OCB molecules may have a different mutual alignment in the high temperature nematic phase*.

(vi) The dielectric anisotropy ($\Delta\epsilon = \epsilon_\parallel - \epsilon_\perp$) which is strongly positive for pure 8OCB decreases as the concentration of BC molecules is increased (see Figure 3.10). The BC molecules are not as strongly polar as 8OCB molecules, and further, the dipole moment of the molecule is along the arrow axis(Figure 3.1) which orients perpendicular to the director in the nematic phase, as we shall describe later.

(vii) The dielectric anisotropies ($\Delta\epsilon$) of pure 8OCB and all the mixtures are positive and increase
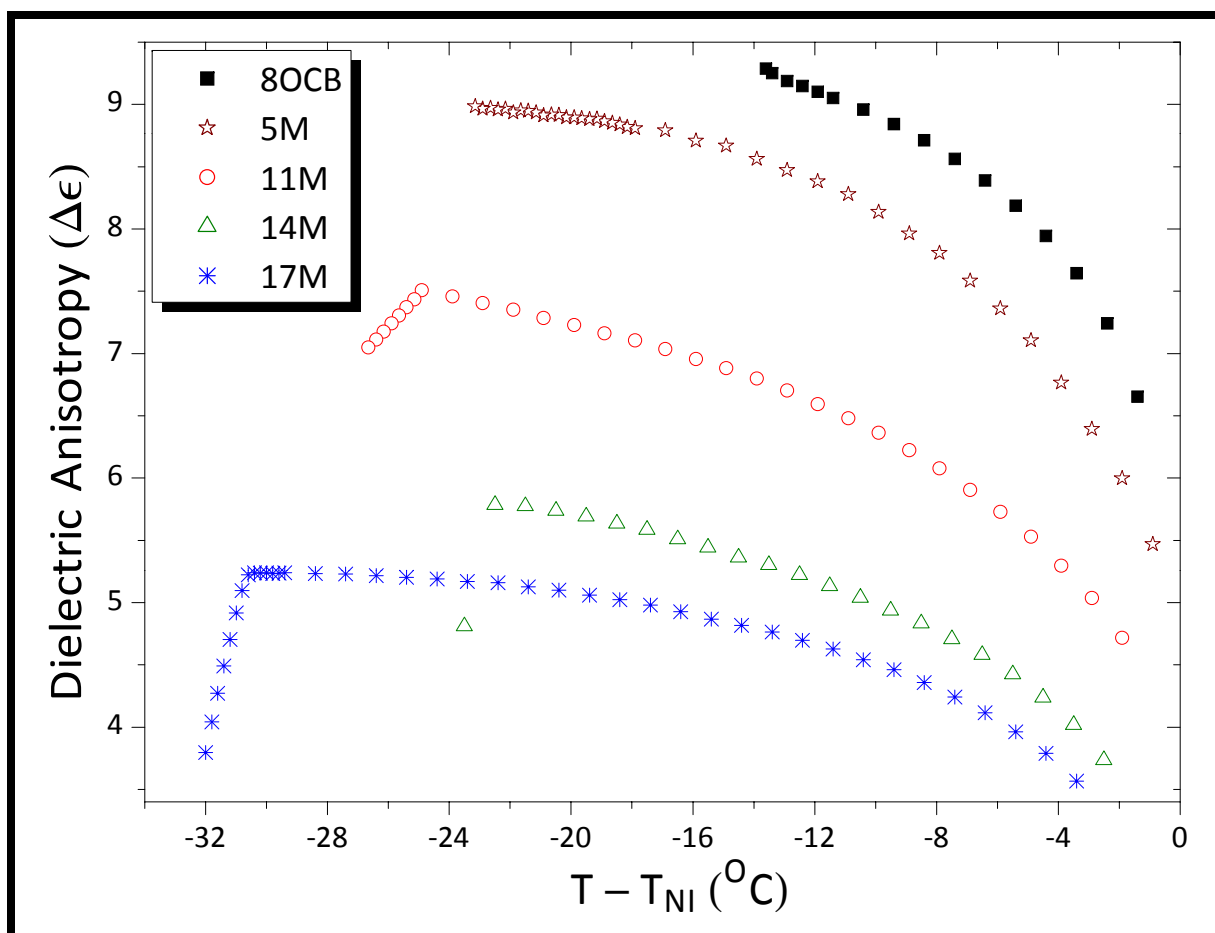
FIGURE 3.10: Dependences of $\Delta\epsilon$ of pure 8OCB and four mixtures on the relative temperatures.

with decrease of temperature except close to T_{AN} (Figure 3.10).

The main difference in the temperature variation of $\Delta\epsilon$ of 8OCB and the mixtures is seen on approaching the N-SmA$_d$ transition temperature(Figure 3.10). In 8OCB, $\Delta\epsilon$ is *enhanced* as the smectic like short range order builds up which leads to an enhancement in the orientational order parameter[1]. In 5M mixture, $\Delta\epsilon$ reaches a broad maximum and saturates. However, in all other mixtures with >11 Mol% of BC molecules, $\Delta\epsilon$ exhibits an anomalously sharp *decrease* as the N-SmA$_d$ transition point is approached. The temperature at which this drop starts corresponds to that at which the smectic like short range order starts building up. The sharp fall in $\Delta\epsilon$ is associated with that $\epsilon_{\parallel}$. As the temperature is raised in the nematic phase the smectic like short range order is weakened and the temperature

dependence of $\Delta\epsilon$ is reversed, reflecting the influence of the long range orientational order (Figure 3.6). This also means that the mutual alignment of the R and BC molecules is different, and can be expected to be as shown in Figure 3.13a, with the bow axes of BC molecules aligned along the long axes of the R molecules for entropic reasons. The arrow axes of the BC molecules have no preferred orientation in the plane orthogonal to **n**, leading to *uniaxial* symmetry of the N phase.

One consequence of this mutual orientation is seen in the relative temperature variations of $\epsilon_\perp$ of 8OCB and the mixtures. The variation is highest for pure 8OCB(Figure 3.8) and becomes progressively smaller as the concentration of BC molecules is increased. The transverse dipoles of BC molecules contribute better to $\epsilon_\perp$ as the orientational order parameter is increased, slowing down the reduction in $\epsilon_\perp$ at lower temperatures.

3.3.3 Elastic Constants :

(i) Figure 3.11 shows K_{11} as a function of temperature for 8OCB and four mixtures. In all the mixtures K_{11} increases with decrease in temperature except close to the N-SmA transition point. As the concentration of BC molecules is increased, K_{11} decreases. Very close to the nematic-isotropic transition temperature, K_{11} of pure 8OCB, 5M and 11M are similar. Only as the temperature is decreased K_{11} of 5M becomes lower than that of 8OCB and K_{11} of 11M is even lower. In 11 M mixture K_{11} decreases by about 10% from that corresponding to 8OCB at 10°C below the isotropic-nematic transition point. The BC molecules have a lower symmetry compared to 8OCB molecules, and the addition of BC molecules makes it easier to produce elastic deformation of the director.

(ii) In all the mixtures the temperature dependence of K_{11} changes sign and K_{11} *decreases sharply* close to the N-SmA transition point (see Figure 3.11). This reflects the reorientation of BC molecules in the smectic-like short range ordered (SRO) groups. As shown in Figure 3.13(b) the bent nature of the molecules can aid the splay deformation in the smectic like short range ordered groups in the nematic phase.

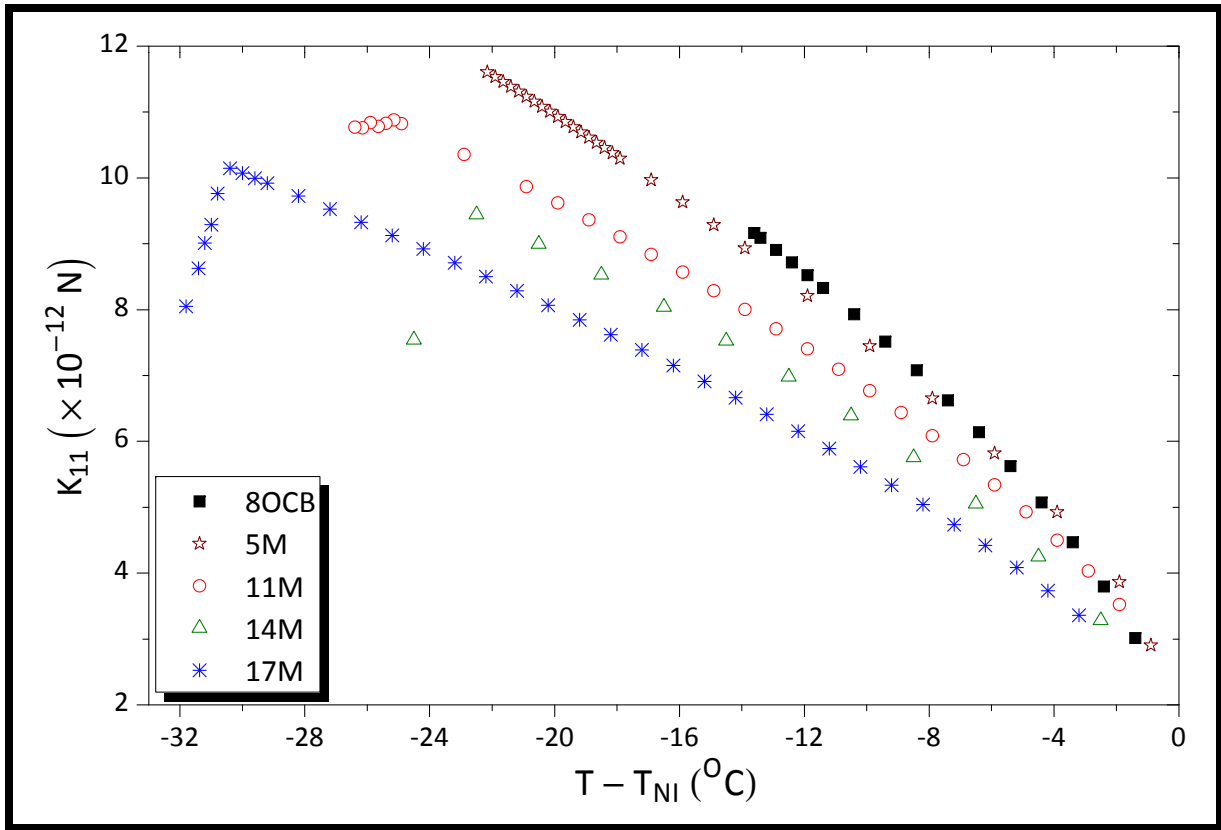(iii) The bend elastic constant K_{33} decreases with the concentration of BC molecules. In 11

FIGURE 3.11: Dependences of K_{11} of pure 8OCB and four mixtures on the relative temperatures.

M mixture K_{33} decreases *four times* from that corresponding to 8OCB at 10°C below the isotropic-nematic transition point (see Figure 3.12). This reduction is much more than the reduction of K_{11}.

(iv) K_{33} also behaves **anomalously** with temperature. K_{33} initially increases and reaches maximum in 14M and 17M mixtures and then decreases slowly as the temperature is lowered from T_{NI}. Close to nematic-smectic transition point, K_{33} again increases.

The molecules are bent and when there is a bend deformation they can more easily get accommodated with the director field of the rods. The bend elastic constant decreases by the presence of BC molecules in the medium. As the temperature is lowered the order parameter increases and the influence of BC molecules becomes even stronger. Instead of the bend constant increasing with that of the orientational order, it actually *decreases*. Very close to N-SmA transition point K_{33} shows an increasing trend, because of the build
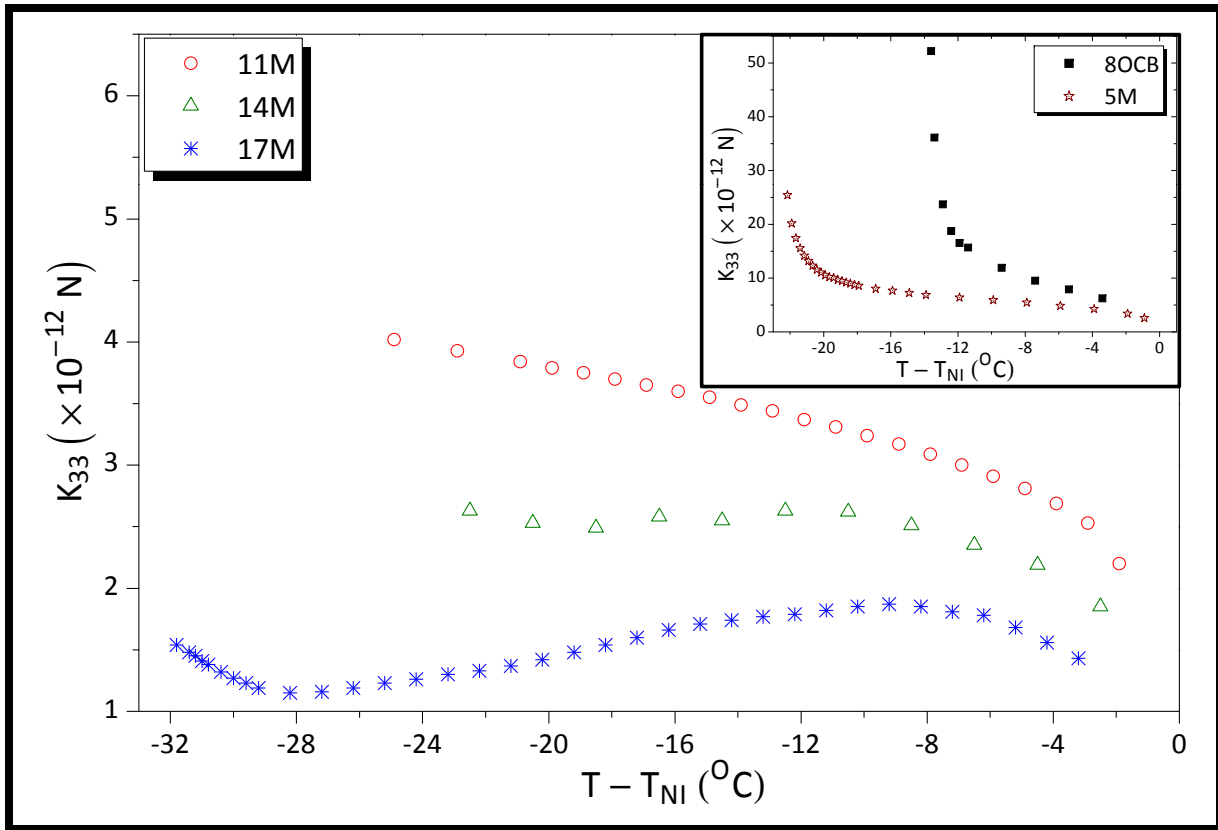
FIGURE 3.12: Dependences of K_{33} of pure 8OCB and four mixtures on the relative temperatures. The data for 8OCB and 5M mixture are shown in the inset.

up of smectic like SRO. In this case, the bend distortion of the director field becomes more difficult, as is well known[1, 2].

3.4 Analysis of Temperature Dependences of Elastic Constants

In the 17M mixture the decrease of K_{11} is by about 35% from that corresponding to pure 8OCB(Figure 3.11). The *bent-shape* of the BC molecules which are aligned with the rods as shown in Figure 3.13a in the N phase, lowers the splay elastic constant[37].

The curvature elastic constants of a nematic owe their origin to the orientational order parameter S. Indeed in the mean field theory, $K_{ii} \propto S^2$. However, other temperature dependent
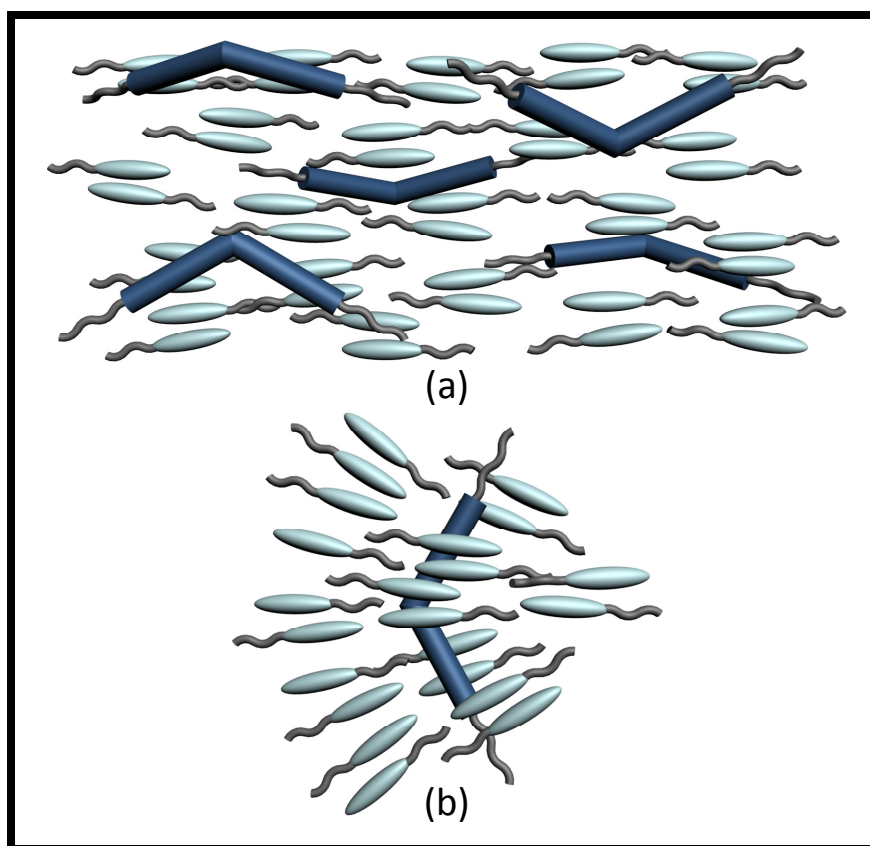
FIGURE 3.13: (a) Mutual alignment of R and BC molecules in the nematic phase (b) BC molecules reorient when smectic like short-range order builds up. The bent core molecules favour a splay distortion of the director field dominated by rods.
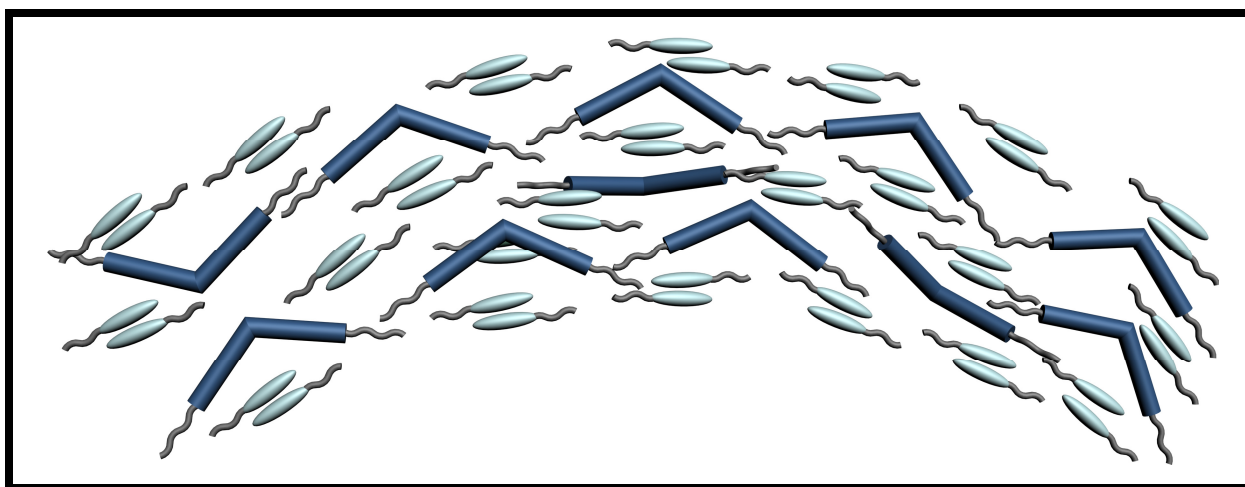

FIGURE 3.14: In the nematic phase the BC molecules fit very well in a director field with bend distortion.

Sample	C_{11}	β_{11}
8OCB	37.8	2.67
5M BC12	48.5	2.54
11M BC12	37.6	2.24
14M BC12	36.2	2.52
17M BC12	34.4	2.63

Table 3.2: Estimated values of C_{11} and the index β_{11} as in Equation (3.2) for 8OCB and four mixtures.

properties like short range smectic like order in the medium also influence the elastic constants, especially the twist and bend constants. We have fitted the K_{11} data which is not close to T_{AN} by the following equation :

$$K_{11} = C_{11} S^{\beta_{11}} \tag{3.2}$$

where C_{11} and β_{11} are two fit parameters. The parameter values are listed in Table 3.2. C_{11} shows a non-monotonic behaviour with concentration of BC molecules. It increases from 8OCB to 5M and then decreases continuously. This reflects the trend in Δn_0 (see Table 3.1). $\beta_{11} \simeq 2.4 \pm 0.2$ which is somewhat larger than the mean field value. The data points and the fitted curves for all the samples are shown in Figure 3.15.

In the case of 8OCB, K_{11} continues to increase up to T_{AN}. But in the mixtures the trend is very different close to T_{AN}, and K_{11} starts to *decrease sharply*. As in the case of $\Delta\epsilon$, the rapid fall in K_{11} arises when the smectic like SRO builds up and the mutual orientation of the two types of molecules is as shown in Figure 3.4. *The bent-shape of BC molecule can in turn distort the local smectic like short range layering to produce a splay distortion of the director* (Figure 3.13b). *As a result the splay elastic constant can drop and show the* **anomalous** *temperature dependence* close to T_{AN}. In the SmA_d phase itself, the layers can be expected to become flat as in Figure 3.4.

In pure 8OCB and 5M mixture as T_{AN} is approached K_{33} *diverges* because the smectic-like SRO builds up (Figure 3.12 inset) [1, 2]. In the case of 11M mixture, K_{33} increases with decrease
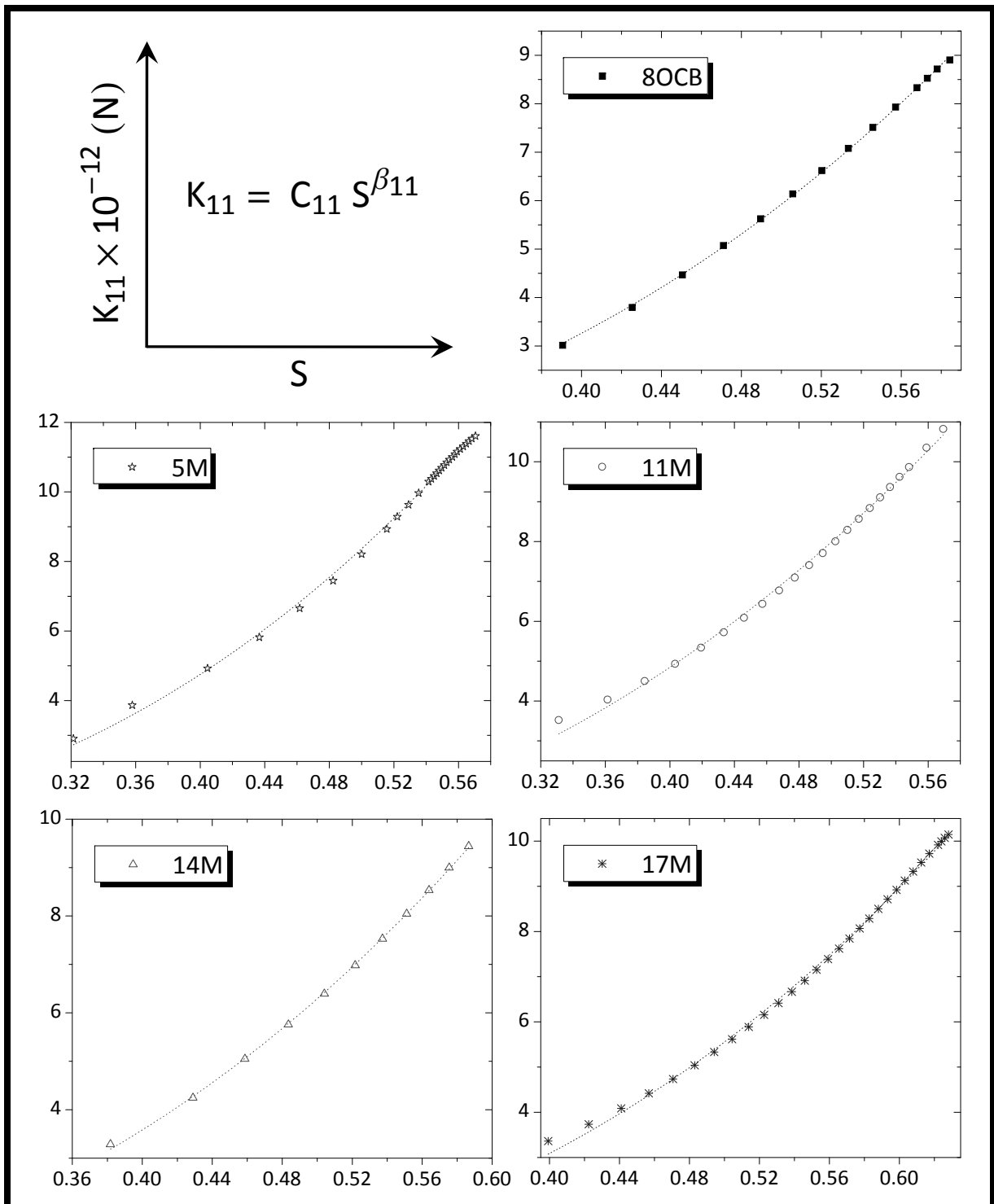
FIGURE 3.15: K_{11} Vs. order parameter (S) of pure 8OCB and four mixtures fitted with Equation (3.2).

of temperature in the N range and we do not have data close to T_{AN}. As the concentration of BC molecules is increased to 14M, K_{33} shows a maximum followed by a *small reduction* as the temperature is lowered, and again increases close to T_{AN}. The **anomalous** decrease of K_{33} with decrease of temperature becomes very prominent in the case of 17M mixture. The maximum and minimum values of K_{33} are 1.8×10^{-12} N and 1.2×10^{-12} N respectively, i.e. the decrease is by about 40% from the maximum value. In 8OCB, at all temperatures, $K_{33} > K_{11}$. In all the mixtures, $K_{33} < K_{11}$ and at $T_{NI} - T = 28°$ C, the 17M mixture has $K_{33} \sim 0.1\,K_{11}$. The order parameter itself increases monotonically as reflected in the variation of Δn with decrease in temperature in all the mixtures(Figure 3.7). However, with the enhanced orientational order of the BC molecules, their bent-shape can *couple better* to the bend distortion of the director, thus decreasing K_{33}. Only near T_{AN}, the build up of smectic-like SRO again gives rise to an increase in K_{33} as the bend distortion of **n** is not compatible with layering order. However in view of the mutual alignment of the two types of molecules being as shown in Figure 3.13b, the enhancement of K_{33} due to the short range smectic order is not as pronounced as in pure 8OCB.

As we have mentioned earlier, in the mean field model, far above T_{AN},

$$K_{ii} = K_i^0\,S^2 \qquad\qquad (i = 1,\ 3) \qquad\qquad (3.3)$$

For pure 8OCB, we set

$$K_3^0 = K_3^r \qquad\qquad (3.4)$$

However, we found in the case of splay constant, $K_{11} \propto S^x$ with $x > 2$. Nevertheless we will use Equation (3.3) for the sake of simplicity to hold good in the case of bend constant.

In the mixture with a *small mole fraction C_b* of BC molecules, we can write

$$K_3^0 = (K_3^r - \alpha_3\,C_b) \qquad\qquad (3.5)$$

giving rise to a reduction of K_{33} as C_b is increased. As the coupling between the bent-shape of BC molecule and bend distortion is *enhanced with the order parameter S*, we can further assume that $\alpha_3 = \beta_3 S$. Using this, we can deduce that K_{33} exhibits a maximum at the order parameter[41]
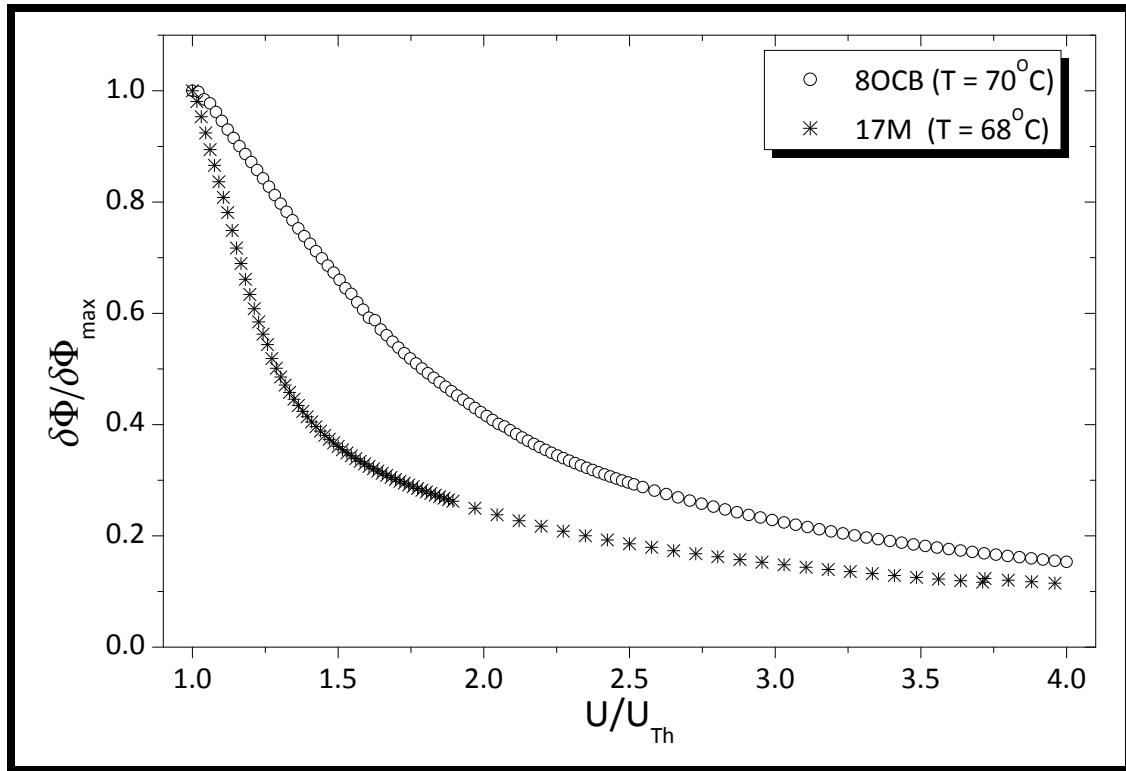
FIGURE 3.16: Normalized optical phase difference $\delta\Phi/\delta\Phi_{max}$ versus normalized voltage U/U$_{Th}$ of pure 8OCB and 17M mixture

$$S_m = \frac{2\,K_3^r}{3\,\beta_3}\,\frac{1}{C_b}$$

(3.6)

The maximum occurs at a lower value of S_m, i.e. at a higher temperature, as C_b is increased, reflecting the experimental trend (Figure 3.12). From our experimental data we estimate that $\beta_3/K_3^r \simeq 6$. Our experiments show that the anomalous temperature dependence of K_{11} close to T$_{AN}$ and that of K_{33} at higher temperatures arise from different mutual alignments of the two types of molecules. Further, the anomaly in K_{33} shows that the coupling between the *bent-shape* of the molecule with the bend distortion of **n** is stronger when the orientational ordering is higher. The anisotropy of elastic properties of the 17M mixture increases to an extremely large value as the temperature is lowered in the N phase, before decreasing again when smectic-like SRO develops in the medium.

We have plotted the normalized optical phase difference $\delta\Phi/\delta\Phi_{\mathrm{max}}$ versus the normalized voltage U/U_{Th} of pure 8OCB and 17M mixture at typical temperatures in the nematic range. (Figure 3.16). $\delta\Phi/\delta\Phi_{\mathrm{max}}$ of 17M decreases far more sharply with increasing field compared to that of pure 8OCB.

As the bend elastic constant of 17M is very small compared to that of pure 8OCB, the bend distortion of the director sharply increases with applied electric field. This also means that the electro optic effect in 17M mixture is much sharper than in pure 8OCB. This sharp electro optic effect is of obvious interest in display applications, for example in multiplexing a large number of lines.

3.5 Measurements on Mixtures with Higher

Concentrations of BC12 Molecules

In view of the anomalous trends in the temperature variations in the elastic constants found in the mixtures with 14 and 17 Mol % BC12 molecules, it is of obvious interest to investigate mixtures with even higher concentrations of BC molecules. As seen in the phase diagram (Figure 3.2) the nematic phase occurs even when the concentration of BC molecules is increased to $\sim$ 45 Mol %. With this in view, we undertook measurements on 24M mixture. We note the following points :

(i) The samples studied in the earlier section underwent transitions from the nematic to SmA_d or SmA_{db} phases, as the temperature was lowered.

(ii) The 24 Mol % sample undergoes a transition to a new type of 2-dimensionally periodic (columnar) liquid crystalline phase called B'_1, which has layering of 8OCB molecules and a periodic arrangement of BC molecules in the layer[14].

(iii) At any relative temperature, the birefringence of mixtures decreases with increasing concentration of the BC compound. Δn of 24M is lower compared to that of other mixtures(Figure 3.17)

(iv) The dielectric constant of the 24M in the isotropic phase is $\sim$ 8.5, which is *much above* that of other mixtures, and almost similar to that of pure 8OCB(Figure 3.18).

(v) $\epsilon_\perp$ which is measured at a low applied voltage of $\sim$ 0.5 V is also *much larger* than that of 8OCB and other mixtures, at any relative temperature (Figure 3.18).

(vi) In the measurement of ϵ as a function of field, for example at $(T - T_{NI}) = -7.2° C$ (Figure 3.19), the dielectric constant continues to be *higher than* that of 17M mixture. Curiously, the *threshold voltage* for 24M mixture is higher than that of 17M mixture, as expected for a medium with a smaller dielectric anisotropy. Near the threshold ($\sim$ 1.3 V) voltage, the *larger value of* $\epsilon_\perp$ apparently leads to a *smaller* $\Delta\epsilon$.

(vii) The extrapolation of ϵ at high voltages to $1/V = 0$ leads to a value of $\epsilon_\parallel \approx 11.0$, which is also much larger than that of 17M mixture ($\epsilon_\parallel \approx 9.7$). If this value is used, $\Delta\epsilon =$
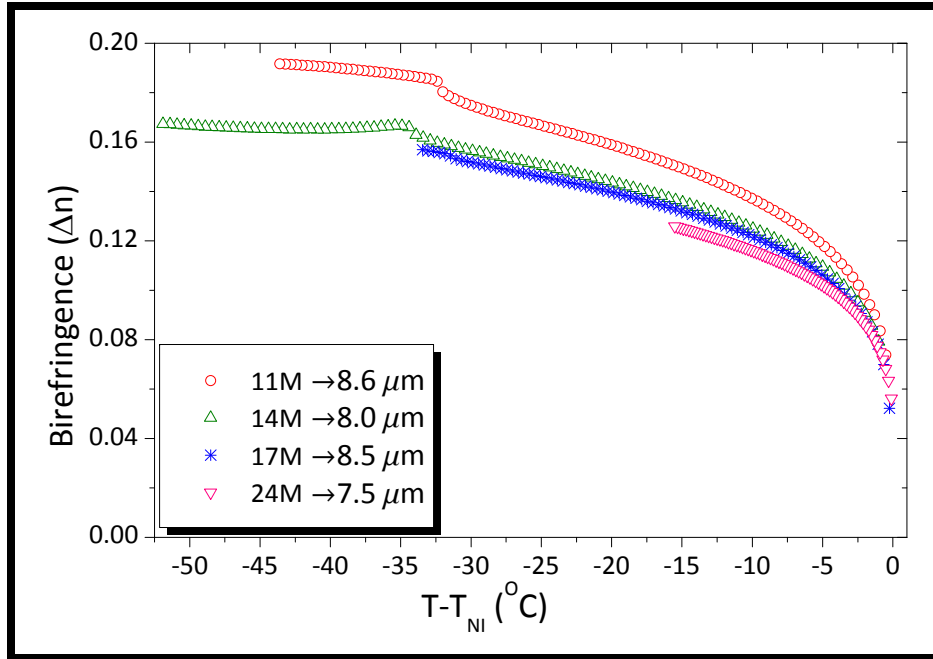
FIGURE 3.17: Dependences of birefringence of four mixtures on the relative temperatures. Thicknesses of the cells are also shown.

$\epsilon_\parallel - \epsilon_\perp \approx 4.3$, is similar to that of 17M mixture in which $\Delta\epsilon$ is measured using the same technique(Figure 3.20). At same relative temperature the Fréedericksz threshold voltage is higher for 24M than that of 17M mixture(see Figure 3.19). This implies that the dielectric anisotropy of 24M should be lower than that of 17M mixture near the threshold voltage. Another feature noted from Figure 3.20 is that $\Delta\epsilon$ of 24M which is similar to that of 17M for temperatures above $T - T_{NI} \approx -11°$, *decreases* at lower temperatures.

In order to investigate this trend further, we conducted other experiments. A mixture with 20M of BC molecules was taken in a *homeotropically* aligned cell of thickness 14.8 μm. This mixture undergoes a transition to the SmA$_{db}$ phase. The temperature dependent dielectric constant $\epsilon_\parallel$ was now directly measured using this cell for various applied AC voltages of frequency 5.64 kHz. The results are shown in Figure 3.21 and summarized below.

(i) At an applied voltage of 0.5V, $\epsilon_{iso} \sim 6.5$, which is lower than that of 17M(see Figures 3.8 and 3.21). In the nematic phase, $\epsilon_\parallel$ increases and attains a value of ~ 9.7 at $T - T_{NI} \sim -28°C$, before starting to decrease as the N-SmA$_{db}$ transition point is approached, and finally levels

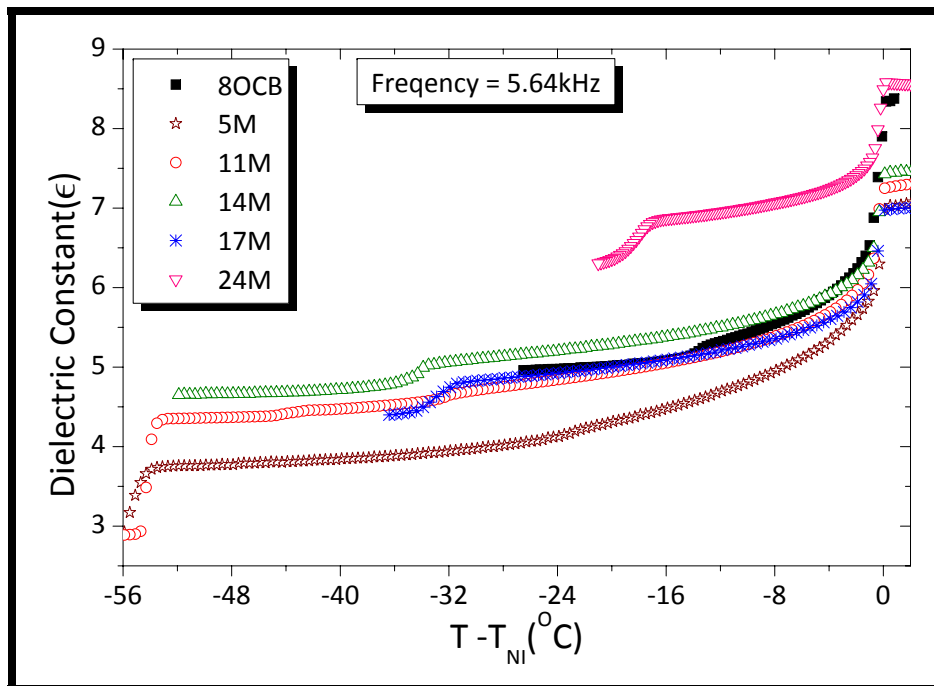Figure 3.18: Dependences of $\epsilon_\perp$ of pure 8OCB and five mixtures on the relative temperatures. $\epsilon_\perp$ of 24M exhibits highest values. Measurements are made at 5.64 kHz.
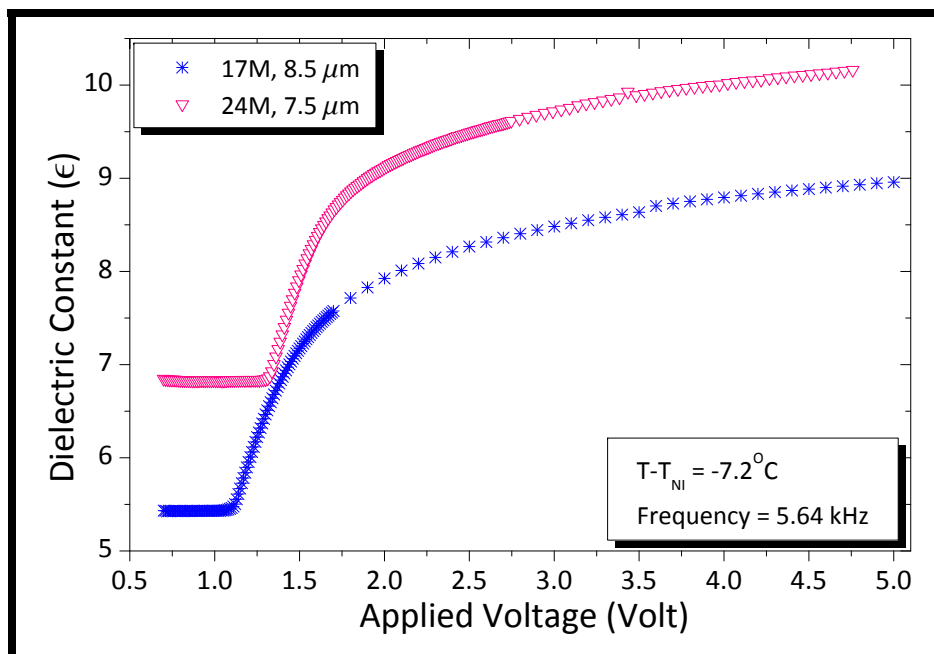

Figure 3.19: Variation of ϵ with applied voltage. $\epsilon_\perp$ and Fréedericksz threshold voltage of 24M are higher than those of 17M mixture.
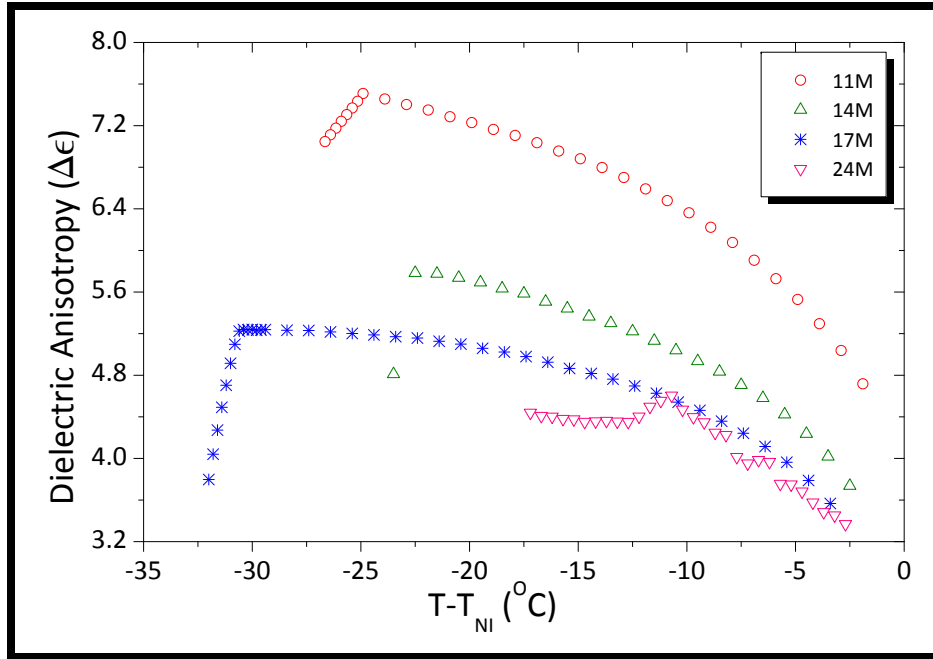
FIGURE 3.20: Dielectric anisotropy of four mixtures. $\Delta\epsilon$ of 24M and 17M are very close at higher temperatures in the nematic range.

off at a value of ~ 9.0 in the SmA$_{db}$ phase. We have already discussed the origin of this lower values of $\epsilon_{\parallel}$ in the smectic phase.

(ii) A similar trend is seen at an applied voltage of 2V, though the dielectric constant is somewhat higher (by $\sim 2\%$) at all temperatures.

(iii) When the voltage is increased to 8V, similar values of $\epsilon_{\parallel}$ are obtained only down to $\sim 76°$C. At this temperature a sudden *increase* of $\epsilon_{\parallel}$ by $\sim 5\%$ is clearly visible(Figure 3.21). As the temperature is lowered further, $\epsilon_{\parallel}$ continues to increase, and as at lower voltages, $\epsilon_{\parallel}$ starts to decrease a few degrees above N-SmA$_{db}$ transition point. Even in the smectic phase, $\epsilon_{\parallel}$ is higher than that at lower voltages.

(iv) At the next higher voltage, *viz.* 10V, even in the *isotropic phase*, ϵ_{iso} shows a *higher value* which is $\sim 6\%$ larger compared to the value measured at lower voltages. In the nematic phase, $\epsilon_{\parallel}$ is higher at all temperatures compared to the values measured at lower applied voltages. As usual, $\epsilon_{\parallel}$ decreases as the temperature is lowered below $\sim 59°$C as the nematic
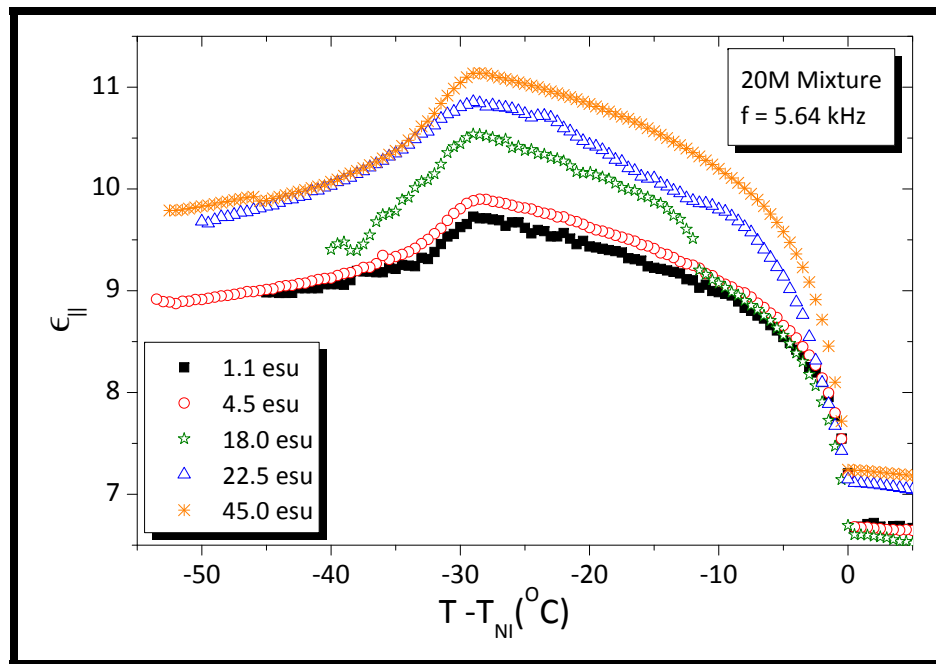
FIGURE 3.21: Temperature variations of $\epsilon_\parallel$ at different applied electric fields of 20M mixture. $\epsilon_\parallel$ increases with increasing electric field. (The field values are given in esu for comparison with measurements on 8OCB which are taken from the literature).

smectic A_d transition point is approached. But even $\epsilon_\parallel$ at low temperatures in the SmA_{db} phase is much higher than the low voltage values(Figure 3.21).

(v) At 20V, ϵ_{iso} as well as $\epsilon_\parallel$ in the nematic phase take even higher values. But in the SmA_{db} phase, the values are similar to the values at 10V(Figure 3.21).

The above results clearly confirms the trends noticed in the 24M mixture in which $\epsilon_\parallel$ was obtained by extrapolating the ϵ data to $1/V = 0$ in a sample which was homogeneously aligned in the field free state. $\epsilon_\parallel$ *strongly* depends on the applied field, increases by $\sim 15\%$ for a voltage of 20V, which corresponds to a modest field of ~ 1.35 V/μm or ~ 45 esu.

The implication of the above result is that there is a structural change in the medium as a function of applied voltage. For comparison we have shown the temperature dependent $\epsilon_\parallel$ of pure 8OCB as functions of applied fields in Figure 3.22 (from reference[42]). $\epsilon_\parallel$ in this case also increases, but the increase is only by $\sim 1.5\%$ for a field which is ~ 612 esu, *ie.,* the increase is about *10 times smaller* than the one measured by us on 20M mixture, for a field which is ~ 14

times *higher*. The increase in $\epsilon_\parallel$ in 8OCB mainly arises from a quenching of director fluctuations because of the electric field[1].

The results on 20M and 24M mixtures point towards a structural change with field in these cases. The BC molecule has a dipole moment of ~ 4 debye pointing *along* the arrow axis. As we discussed earlier, in the higher temperature region of the nematic phase, the bow axes of the BC molecules are aligned along the nematic director defined by the rod-like 8OCB molecules. This mutual alignment is favoured entropically. The dipoles of the BC molecules contribute to $\epsilon_\perp$ in this structure (Figure 3.13a). $\epsilon_\perp$ shows an increasing trend on the average as the concentration of BC molecules is increased above 5M. But the increase shown by the 24M mixture is *remarkably large*(Figure 3.18).
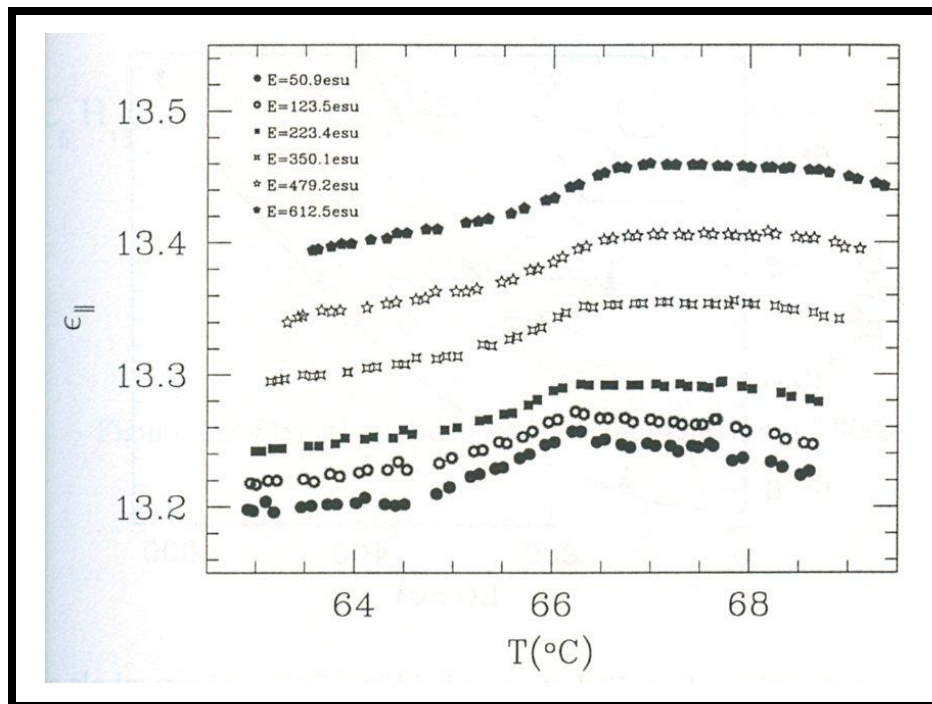

FIGURE 3.22: Electric field dependences of $\epsilon_\parallel$ in 8OCB as functions of temperature (From reference [42], see also [43])

As seen in Figure 3.21, ϵ_{iso} itself has a higher values when the applied field is 22.5 esu. This means the big increase of $\epsilon_\parallel$ observed at 18 esu has brought about a structural change, which persists even in the isotropic phase.

The molecular weight of BC12 is 1142 while that of 8OCB is 307. As the densities of the two compounds are expected to be similar, when the concentration of BC12 exceeds about 20 Mol %, the BC molecules occupy a larger volume than the 8OCB molecules, even though numerically BC molecules are smaller. The mutual interactions between the BC molecules themselves start to prevail especially aided by an external electric field of strength > 18 esu. We believe that the field assisted interaction favours the formation of *clusters*, in which two or more BC molecules are close packed with a common orientation of the arrow axis, thus effectively increasing the dipole moments.

From the Maier-Meier model (see Equations (1.17) and (1.18) of Chapter 1), the orientation contribution to the dielectric constant is $\propto \nu\mu^2$, where ν is the number density of the dipolar units with dipole moment μ. If μ_{BC} is the dipole moment oriented along the arrow axis of one BC molecule, it is clear that by forming a cluster with 2 BC molecules(see Figure 3.23), ν is reduced by 2 while μ is doubled. Thus, the dielectric constant goes up by a factor of 2. This first of all increases $\epsilon_\perp$ by a large value (see Figure 3.18). Further, in the homeotropically aligned sample, the dielectric energy is obviously lowered if these clusters are reoriented such that their dipole moments align along the field direction. Thus, the results imply a reorientation of the BC molecular clusters such that their *arrow axes* are aligned along the 8OCB director under a high field. This is not favoured entropically, but the gain in the dielectric energy ($\propto -\epsilon E^2$) compensates for the loss of entropy already at ~ 18 esu of applied field in the 20M mixture(Figure 3.21).

The results thus bring out two new features in these mixtures : (i) Formation of clusters when the volume fraction of BC molecules is higher than that of 8OCB molecules. Such a cluster formation is already implied by light scattering measurements on pure nematogenic BC molecules even in the isotropic phase[44]. (ii) More interestingly the clusters *reorient* under a moderate field to favour orientations of the arrow axes of the BC clusters along the nematic director.

The effect of the external field on the clusters increases the dielectric constant in *all* the phases, *viz.* isotropic, nematic as well as the SmA$_{db}$ phases. Thus at these higher concentrations of BC molecules, the BC *clusters* are aligned with their arrow axes along the layer normal even in the SmA$_{db}$ phase. The high electric field not only reorients the BC molecules but also favours the formation of clusters.
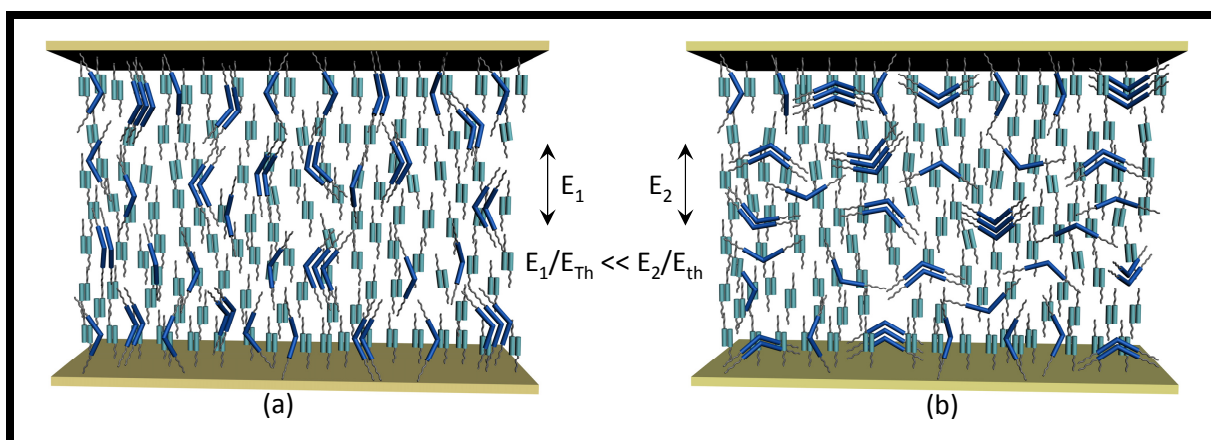
FIGURE 3.23: Clusters of BC molecules in a mixture with high concentration of BC molecules. (a) At the low voltages the clusters are oriented with their bow axes along **n** enhancing $\epsilon_\perp$. (b) In high fields the clusters reorient and the arrow axes align along **n**, enhancing $\epsilon_\parallel$. The optical birefringence measured in a direction perpendicular to the plane of the figure is higher for (a) than for (b).

$\Delta\epsilon = (\epsilon_\parallel - \epsilon_\perp)$ and the short range structure of the liquid crystal itself is now a *function of the applied field*. This alters $\Delta\epsilon$ with field. The field dependent electroptic measurement cannot be used to determine K_{11} and K_{33} of samples with more than ~ 17 Mol% of BC molecules.

In order to confirm that there is a reorientation of the BC clusters by an independent study, we measured the optical anisotropy of a homogeneously aligned sample, as a function of an electric field applied parallel to the director (see Figure 3.24). The field is applied in a gap of 200 μm etched in the lower ITO coated glass plate. SiO evaporated on this plate as well as the upper glass slide ensured a planar alignment of the director **n** parallel to the applied field. The thickness of the sample was $\sim 11.2\mu$m. The optical path difference was measured by using a $\lambda/4$ compensator and taking the readings visually. As there is a considerable error in locating the analyzer orientation to get minimum intensity, 5 readings were taken at each voltage and the average path difference as a function of field is shown in Figure 3.25, for a 24M mixture, at 82°C. Similar field dependences were measured at other temperatures in the nematic phase.

The path difference initially *decreases* with the AC fields. We believe that it reflects the tendency of the BC molecular clusters to reorient along the field, as shown in Figure 3.23. The contribution of the polarizability anisotropy of the BC molecules to the optical path difference is higher when they are oriented as shown in Figure 3.23a than in Figure 3.23b. As the voltage
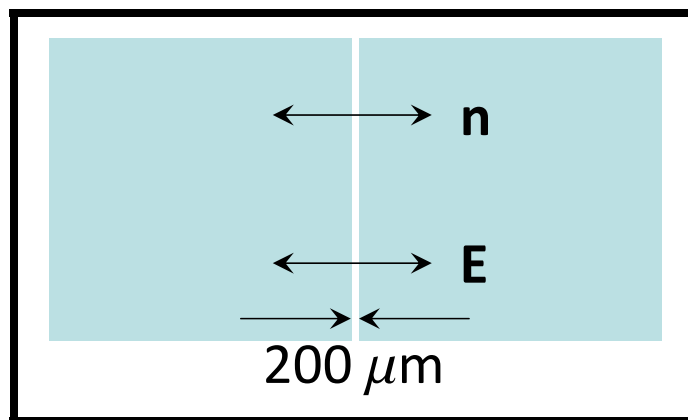
Figure 3.24: Bottom plate of the SiO coated planar cell. Shaded regions indicate conducting ITO coating. The two regions are separated by a gap of 200 μm.

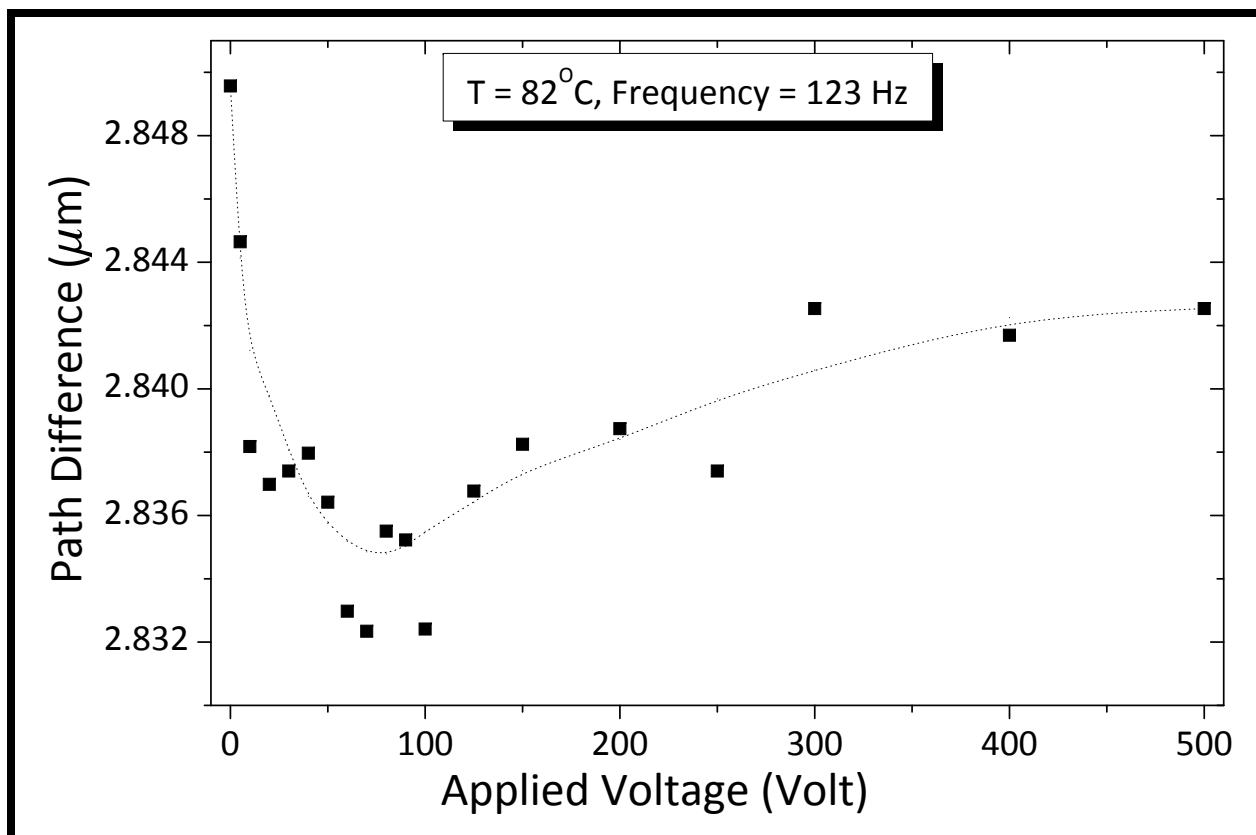Figure 3.25: Voltage dependence of optical path difference in 24M at 82°C.

exceeds ~ 100 V, the path difference again increases. The cluster formation does not change the polarizability anisotropy compared to that of individual BC molecules. Thus the optical effect is relatively small due to the reorientation of the clusters compared to the effect on the low frequency dielectric constant. The increase in path difference at high voltages arises from a field quenching of director fluctuations as in the case of 8OCB.

3.6 Conclusions

The measurements presented in this chapter bring out several novel results on the properties of the mixtures of 8OCB and BC12. In the nematic phase, the bow axes of the BC molecules align along the director defined by the long axes of 8OCB molecules for entropic reasons at temperatures well above T_{AN}. This lowers both the splay and bend elastic constants compared to those of pure 8OCB. K_{33} exhibits an anomalous decrease with decreasing temperature in 14M and 17M mixtures, as the bent shape of the BC molecule couples to the bend distortion of the director more strongly when the orientational order parameter is higher. In all the mixtures, $K_{33} < K_{11}$. As the N-SmA$_d$ transition point is approached, the smectic like short range order builds up, and the BC molecules reorient and their arrow axes align along the director. This gives rise to a sharp reduction in K_{11} as well as $\epsilon_\parallel$. In 20M and 24M, the volume fraction of BC molecules exceeds that of 8OCB and the mutual interactions between BC molecules becomes dominant. This leads to the formation of clusters of 2 or more BC molecules, which enhance $\epsilon_\perp$ in 24M to high values. In 20M a sufficiently large electric field applied along the director reorients the clusters such that their arrow axes point along the field direction, which increases $\epsilon_\parallel$. This field induced reorientation has been confirmed by optical studies on the 24M mixture.

In rod-like molecules with a large longitudinal dipole moment like 8OCB, the electrostatic interaction between neighbouring molecules favours an antiparallel orientation[45], thus ensuring the apolar nature of the director. On the other hand, in BC molecules with dipole moments along the arrow axes, a *parallel* orientation as shown in Figure 3.23 is favoured both due to packing effects and electrostatic interactions, thus leading to the formation of highly polar clusters.