

CHAPTER 8

**Preparation and comparative study
of the electro-optic properties of
binary mixtures of orthoconic anti-
ferroelectric esters and achiral
phenyl pyrimidine liquid crystal**

8.1 Introduction

Recently liquid crystals with ferro and anti-ferroelectric ordering have emerged as very promising ‘smart materials’ due to their sensitivity to external stimuli such as electric and magnetic field. In the ferroelectric smectic C* (SmC^*) and anti-ferroelectric smectic C* (SmC_A^*) liquid crystal phases, the molecules are closely packed within the smectic layers and additionally, the director tilt with respect to the layer normal makes all these phases locally polar, as a result of which every smectic layer carries a nonzero spontaneous polarization in the layer plane [1]. In a surface stabilized configuration, between the rubbed polyimide-coated glass slides, due to coupling of the spontaneous polarization (P_s) with the electric field (\sim volts per micron), ferro (SmC^*) and anti-ferroelectric (SmC_A^*) liquid crystals acts as a fast switching electro optical light valve [2,3]. These light shutters are expected to revolutionize the field of commercial high-resolution reflective micro displays [4], nonlinear optics, three level phases only modulators [5] and other high speed technological applications [6]. Especially, the orthoconic anti-ferroelectric liquid crystals [7-9] have been attracting a great deal of attention due to their unique properties such as ideal dark state, fast response time, wide viewing angle, easy gray scale switching and absence of surface treatment. However, the high viscosity of the SmC^* and SmC_A^* phase have resulted in response times that are too long for commercially acceptable surface stabilized ferroelectric liquid crystals display (SSFLCDs). To overcome this drawback normally an achiral smectic C compound with a low viscosity, high smectic C phase transition temperature and low melting point has been doped into a chiral liquid crystalline (LC) compound with a very high value of P_s to improve the electro-optic and optical properties of the LC mixture. The pyrimidine based achiral liquid crystals are relatively less viscous [10] and exhibit a wide stable SmC phase. Moreover, the electron withdrawing character and its ability to be easily functionalized make the pyrimidine derivatives promising candidates for such type of mixture formulation [11-14]. The mixing of two mesogens that are quite different from each other can strongly alter the properties and the phase

behaviour of the mixtures, compared to the pure compounds. Therefore, liquid crystal mixtures with desired properties have been optimized to improve the performance of the SSFLCDs than the single-component liquid crystals.

In this work characterization using microscopic observations and electro-optical methods has been applied to deduce the phase behaviour and physical properties (*viz.* spontaneous polarization, relaxation time, effective torsional viscosity, anchoring energy coefficients etc.) of some binary mixtures comprising of non-ferroelectric phenyl pyrimidine and orthoconic antiferroelectric liquid crystals for high speed applications. Additionally, this study also reveals the fundamental aspect of chiral perturbations in the environment of an achiral liquid crystalline system and their intermolecular interactions in the binary mixtures.

8.2 Materials

The mesomorphic properties of some analogues of (S)-MHPOBC have been studied extensively by the electro-optical method and described in details in the previous chapter [15]. Some of the investigated compounds with large spontaneous polarization [16-23] and low relaxation time seem to be interesting for mixture formulation for application in surface stabilized orthoconic antiferroelectric liquid crystal (SSOAFLC) displays. In this chapter a systematic study of the binary mixtures of chiral (compounds **HH**, **FH**, **FF**) and an achiral phenyl pyrimidine mesogen (compound **PhP**) have been reported [24]. The chemical structures and the phase transition temperatures of the individual components of the mixtures are listed in Table 8.1. Eleven mixtures has been prepared having mole fraction of **HH** equal to 0.207, 0.402, 0.603, 0.805; **FH** equal to 0.202, 0.409, 0.598, 0.836 and **FF** equal to 0.202, 0.409, 0.597 respectively. The chiral compounds have partially fluorinated terminal chain and six oligomethylene spacer length but the position of the fluorine substituent in the rigid core are different. As shown in Table 8.1, these orthoconic antiferroelectric pure liquid crystals show the phase sequence: Cr-SmC_A*-SmC*-SmA-Iso. The achiral component with short molecular length exhibits the typical liquid-crystalline phase sequence: Cr-SmC-SmA-N-Iso. This broad ranged SmC

mesogen has been chosen for better phase stabilization.

Table 8.1 Chemical structure and phase transition temperature of the pure components of the binary liquid crystalline mixtures.

Sl. No.	Comp.	Chemical Structure (Transition Temperatures)
1	HH	$\text{C}_3\text{F}_7\text{CH}_2\text{OC}_6\text{H}_{12}\text{O}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{COOC}^*\text{H}(\text{CH}_3)\text{C}_6\text{H}_{13}$ Cr 60.5°C SmC _A * 94.7°C SmC* 125°C SmA 126.3°C Iso
2	FH	$\text{C}_3\text{F}_7\text{CH}_2\text{OC}_6\text{H}_{12}\text{O}-\text{C}_6\text{H}_3(\text{F})-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{COOC}^*\text{H}(\text{CH}_3)\text{C}_6\text{H}_{13}$ Cr 57.3°C SmC _A * 80.1°C SmC* 108.5°C SmA 112.7°C Iso
3	FF	$\text{C}_3\text{F}_7\text{CH}_2\text{OC}_6\text{H}_{12}\text{O}-\text{C}_6\text{H}_3(\text{F})_2-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{COOC}^*\text{H}(\text{CH}_3)\text{C}_6\text{H}_{13}$ Cr 62.6°C SmC _A * 84.8°C SmC* 110.5°C SmA 112.8°C Iso
4	PhP	$\text{C}_8\text{H}_{17}-\text{O}-\text{C}_4\text{H}_3\text{N}_2-\text{C}_6\text{H}_4-\text{O}-\text{C}_6\text{H}_{13}$ Cr 43°C SmC 88°C SmA 95.7°C N 98°C Iso

8.3 Phase transition temperatures

Mesophases has been identified by observing the microscopic texture of the compounds under polarizing optical microscope (Motic BA300) equipped with a Mettler Toledo FP90 hot stage and with the aid of polarization reversal current response. The phase sequence and corresponding transition temperatures for the three distinct chiral-achiral binary liquid crystal mixtures are illustrated in Figure 8.1(a-c). The characteristic polarising optical microscopy (POM) textures of different mesophases of binary mixture with mole fraction $x_{\text{HH}}=0.805$ are shown in Figure 8.2(a-c).

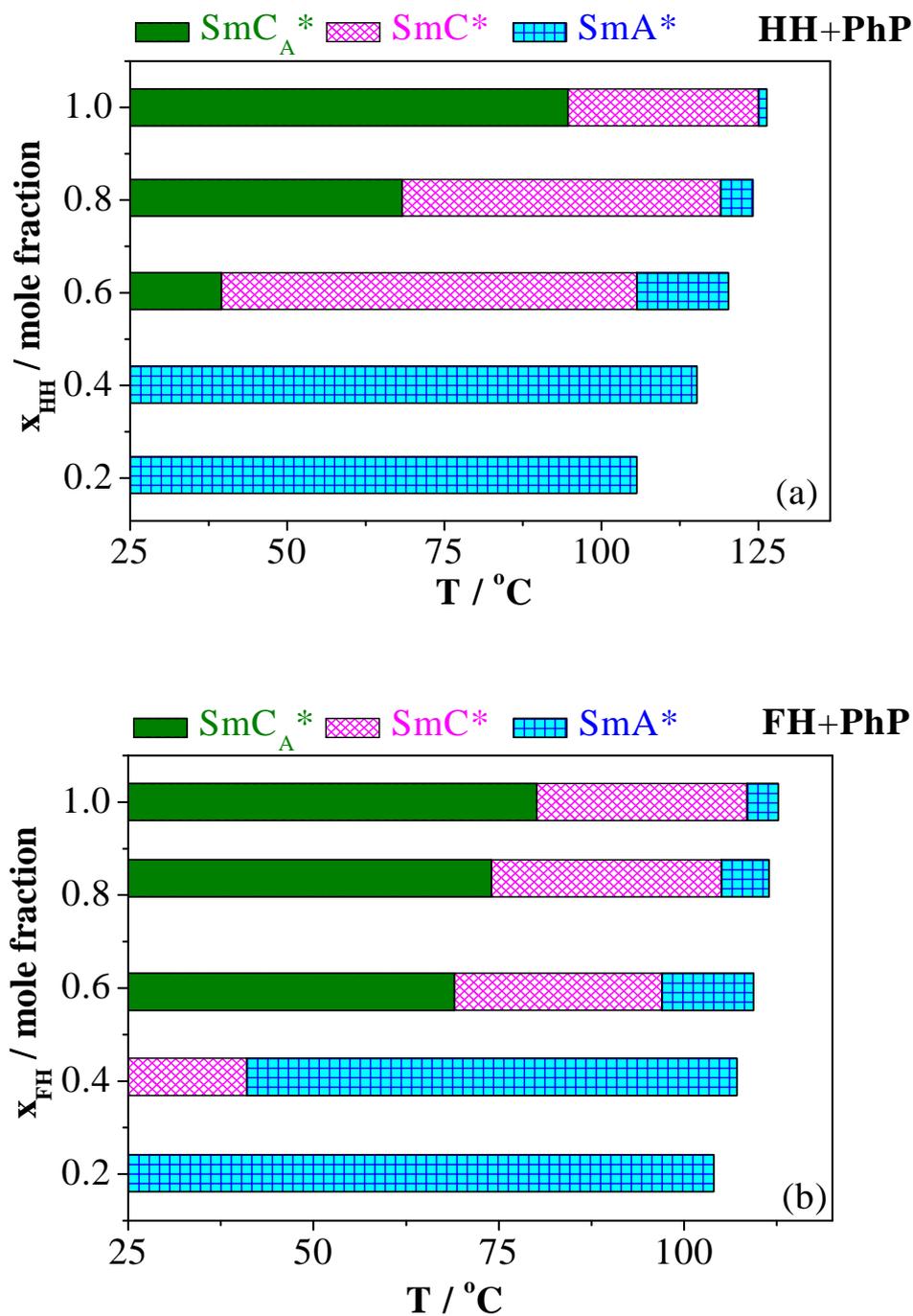


Figure 8.1(a-b) Phase transition temperatures of binary systems (a) **HH+PhP** and (b) **FH+PhP**.

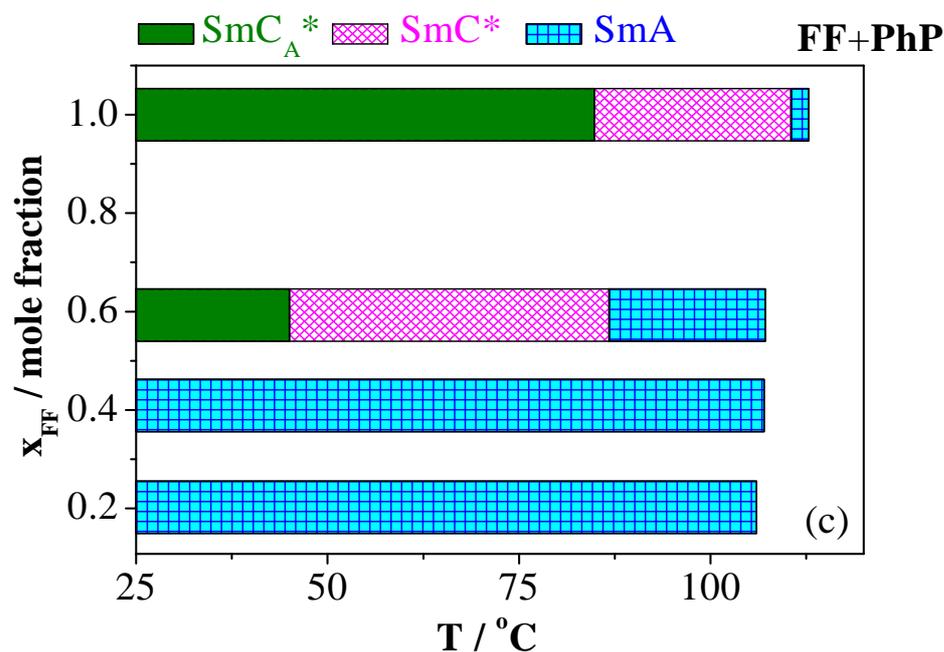


Figure 8.1(c) Phase transition temperatures of binary system **FF+PhP**.

Generally, the pyrimidine mesogens favors smectic C (SmC) phase formation than nematic (N) ones, with lower transition temperatures and melting points. For the wide range of mesophase, these compounds are used in ferroelectric mixture formulation for technological applications [10, 25, 26]. It is observed that the N and SmC temperature ranges of the chiral-achiral mixtures are progressively reduced with increasing proportions of chiral compounds. The N and SmC phase disappears at $x_{(HH/FH/FF)} \geq 0.2$. In the concentration region $0.2 \leq x_{(HH/FH/FF)} \leq 0.4$ these mixtures exhibit only SmA phase in the entire mesomorphic range except for $x_{FH} = 0.4$ (where an additional SmC* phase exists). In SmA phase, fan shaped focal conic texture appears as shown in Figure 8.2(a). The chiral compounds with longer terminal chain induces ferro and anti ferroelectric ordering in the shorter achiral phenyl pyrimidine compound by stereo- polar coupling. In the binary mixture with concentration $0.6 \leq x_{(HH/FH/FF)} \leq 0.8$ mesophases appear with the sequence Iso-SmA-SmC*-SmC_A*-Cr during cooling. In SmC* phase, a broken focal conic texture develops which on further cooling coalesce to form striped focal conic characteristic texture in the SmC_A* phase (Figure 8.2(b-c)).

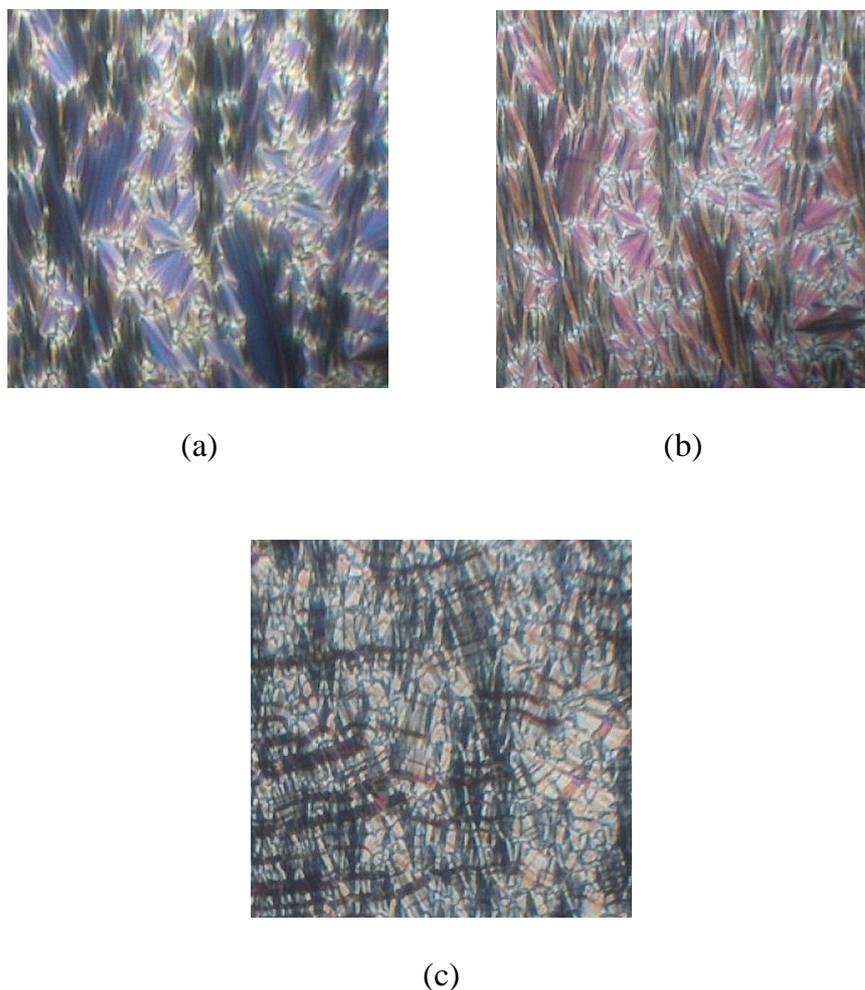


Figure 8.2(a-c) Microphotographs (magnification 400x) of the microscopic pattern for binary mixture ($x_{\text{HH}}=0.8$) during cooling: in (a) SmA phase transition at 120°C, (b) SmC* phase at 90°C and (c) SmC_A* phase at 56°C.

From the transition temperatures of the mixture under investigation it is observed that clearing points of these mixtures show a linear relationship with the concentration of chiral compounds. For the bi-component system (**HH+PhP**), antiferroelectric phase SmC_A* is found to exist over a broad temperature range in comparison to the two other systems. This observation indicates that the lateral fluorination significantly affects the packing arrangement of the liquid crystalline molecules and types of mesophases formation [27]. However both the SmA and

SmC* phase stability is enhanced in these mixtures in comparison to the pure chiral components.

8.4 Spontaneous polarization measurement

The spontaneous polarization (P_s) values have been plotted as a function of reduced temperature (T/T_C) from the Curie point T_C (SmA-SmC* transition) in Figure 8.3. The behaviour of spontaneous polarization with temperature is typical for this kind of liquid crystal mixtures, rising continuously from zero at the SmA to SmC* transition, and tending towards a saturated value at lower temperature.

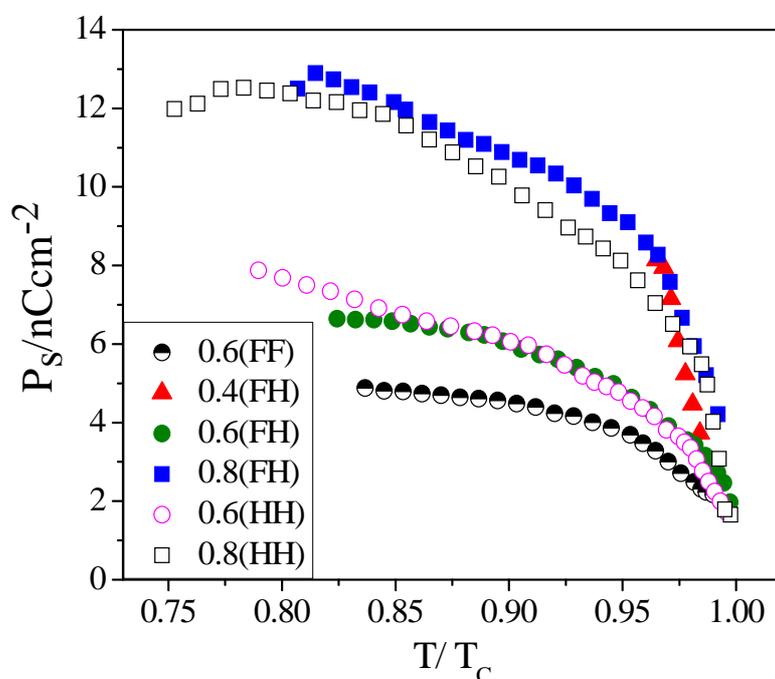


Figure 8.3 Experimental values of spontaneous polarization as a function of reduced temperature for six binary mixtures: 0.6(**FF**), 0.4(**FH**), 0.6(**FH**), 0.8(**FH**), 0.6(**HH**) and 0.8(**HH**).

For all the investigated binary mixtures, the values of the spontaneous polarization drop quite abruptly at the SmC*-SmA phase transition than that of pure orthoconic compounds **HH**, **FF** and **FH**. The P_s values reduce as the achiral concentration increases. This behaviour may be due to the dilatation effect on the

spontaneous polarization by addition of achiral **PhP** compound. Moreover, it may also be due to a reduction in the core-core correlation due to weak anchoring of the shorter terminal chains of achiral **PhP** in the smectic layers [28-31]. A greater mismatch of the alkyl/alkoxyl chain lengths between the **PhP** and chiral compounds also leads to a decrease in the P_s values [32,33]. Binary mixtures with mole fraction $x_{HH}= 0.603$ and $x_{FH}= 0.598$ show higher values of spontaneous polarization in comparison to binary mixtures with mole fraction $x_{FF}= 0.597$ which is consistent with the result discussed in the previous chapter. It is to be noted that in the case of high P_s values an optical hysteresis occurs, which leads to the so-called "ghost images". Therefore the problem of the optical hysteresis may be eliminated by the use of these FLC mixtures having low P_s values. These mixtures may exhibit higher pitch as the value of pitch is almost inversely proportional to spontaneous polarization [34]. Increasing the pitch might lead to improved response times and cancellation of asymmetric response. It also enables easier depression of twisted structure in the cell. The temperature dependence of the spontaneous polarization (Figure 8.3) have been fitted using the following expression [35]:

$$P_s = P_0(T_C - T)^\beta \quad \text{for } T < T_C \quad (8.1)$$

where, T_C is the SmC*-SmA phase transition temperature, β and P_0 are adjustable parameters. The corresponding fitting parameters so determined have been listed in Table 8.2.

The critical exponent β is in the range 0.24-0.31, which is close to the value 0.3125(= 5/16), predicted by the three dimensional Ising model [36]. Therefore, it indicates that the SmC*-SmA phase transition is of second order. However for the mixture ($x_{FF}=0.597$) with laterally di-fluorinated compound **FF**, the β value is close to 0.25, indicating a tricritical mean field behaviour of the SmC*-SmA phase transition [36].

Table 8.2 Fitted parameters P_0 , T_C and exponent β of experimentally determined spontaneous polarization for six binary mixtures.

Mole fraction of mixture	P_0 in nCcm ⁻²	T_C in K	β
$x_{FF} = 0.597$	1.9 ± 0.1	359.9 ± 0.5	0.24 ± 0.01
$x_{FH} = 0.409$	4.5 ± 0.2	309.4 ± 0.4	0.31 ± 0.01
$x_{FH} = 0.598$	2.0 ± 0.1	369.8 ± 0.2	0.30 ± 0.01
$x_{FH} = 0.836$	4.2 ± 0.2	375.8 ± 0.4	0.26 ± 0.01
$x_{HH} = 0.603$	2.0 ± 0.1	377.8 ± 0.2	0.30 ± 0.01
$x_{HH} = 0.805$	3.4 ± 0.1	390.1 ± 0.1	0.30 ± 0.01

8.5 Relaxation time measurement

Figure 8.4 portrays the Arrhenius behaviour of the reduced temperature dependent relaxation time. The relaxation time of the binary mixtures are significantly faster than those of the pure chiral compounds, which is mainly due to the lower rotational viscosities of the phenyl pyrimidine compound **PhP** [37]. The heterocyclic nitro substituent plays a dominant role in promoting chirality transfer in the SmC* and SmC*_A phase and leads to a decrease in the values of the relaxation time τ [38].

The values of the relaxation time have been found to be in the range 50-125 μ s, which makes them attractive for photonics and telecommunication applications. The binary mixture $x_{HH}=0.603$ and $x_{FH}=0.598$ show higher values of the relaxation time than that of $x_{FF}=0.597$. This result suggests that the relaxation time is relatively sensitive to the lateral fluorination in the rigid core of the pure compounds. Introduction of achiral component leads to a stepwise reduction in the τ values from 145 μ s for the pure compound (**HH**) to 74 μ s for $x_{HH}=0.805$, measured at room temperature. Similar observation has been found for the other binary mixtures as well (Figure 8.4).

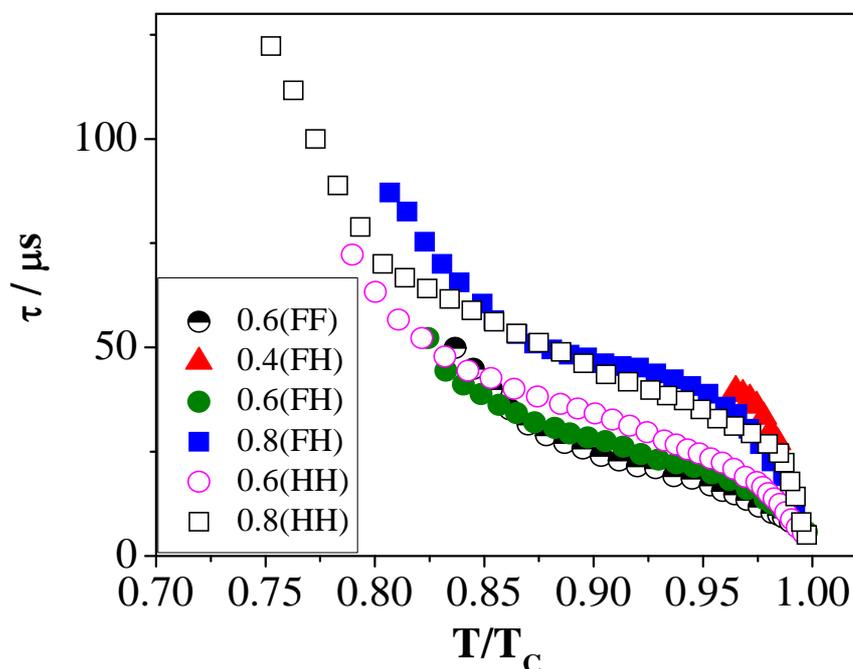


Figure 8.4 Relaxation time (τ) as a function of reduced temperature for six binary mixtures: 0.6(**FF**), 0.4(**FH**), 0.6(**FH**), 0.8(**FH**), 0.6(**HH**) and 0.8(**HH**).

8.6 Effective torsional bulk viscosity measurement

The effective torsional bulk viscosity as a function of the reduced temperature is shown in Figure 8.5. The decrease in effective torsional viscosity with concentration of chiral compounds again shows trend almost similar trend to that of the spontaneous polarization and relaxation time. For all the three systems here, the value of the effective torsional bulk viscosity changes non-linearly with the concentrations of chiral compounds. Intermolecular interaction between the molecules of long chiral ester liquid crystalline compounds and short polar phenyl pyrimidine compound are responsible for the non-additive behaviour of the investigated binary mixture. Such type of interactions can be qualitatively explained using the Boulder model [39,40]. According to this model, the chiral compound behaves as a guest surrounded by the achiral host molecules and perturbs the orientational distribution of the transverse dipole moment of the achiral environment with respect to the polar C_2 axis. Such interactions via core-

core correlations may favour or oppose orientations of the transverse dipole moment along the polar C_2 axis depending on the structural complementarities of the chiral and achiral component of the mixtures [28]. The decrease in the viscosity values with increasing proportion of the achiral component **PhP** gives evidence that the twist states gradually unwind and make the system less viscous.

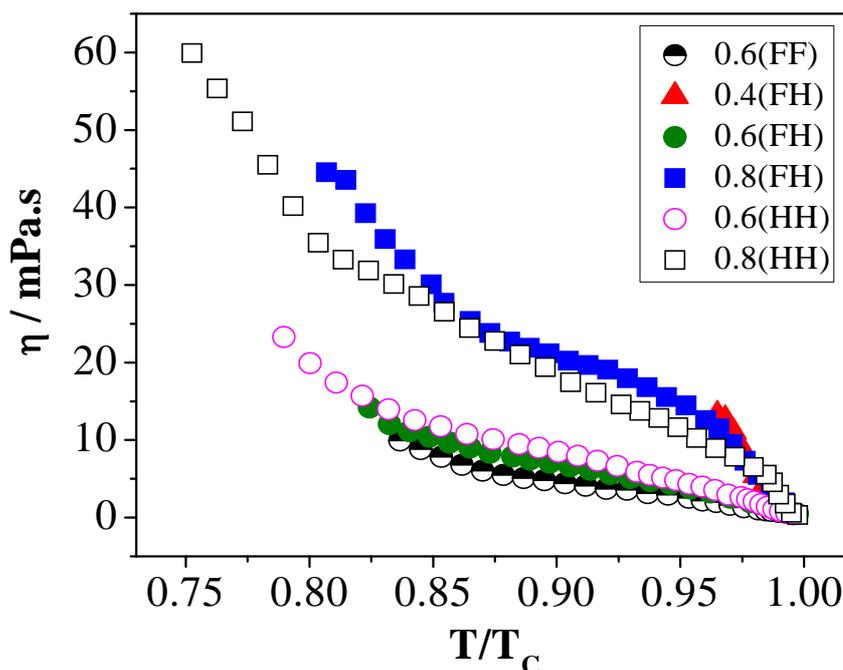


Figure 8.5 Effective torsional bulk viscosity (η) as a function of reduced temperature for for six binary mixtures: 0.6(**FF**), 0.4(**FH**), 0.6(**FH**), 0.8(**FH**), 0.6(**HH**) and 0.8(**HH**).

The width of the pyrimidine ring is wider than the width of the phenyl ring, therefore the molecule is inflated at the centre position which increase the distance between the molecules. As a result the effective torsional viscosity becomes less [41]. Pyrimidine-based calamatic liquid crystals enhance the longitudinal dipole moment of the core without increasing viscosity while a polar substituent at the same position in the rigid core increase the sterical hindrance and induce a higher viscosity. Therefore, pyrimidine-based liquid crystals are more suitable for mixture formulation in high speed display applications. The Arrhenius plot of viscosity has been presented in Figure 8.6.

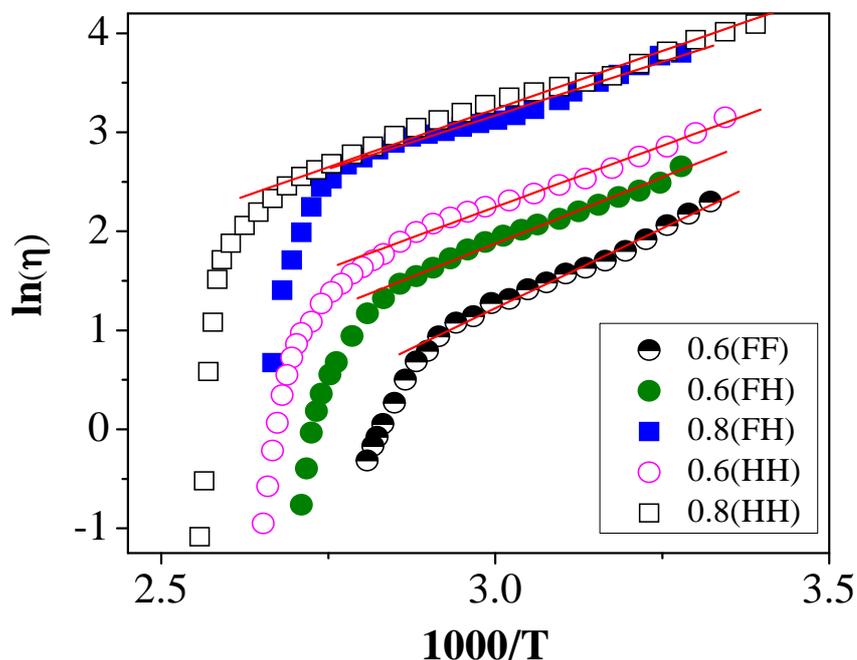


Figure 8.6 Logarithmic plot of the effective torsional bulk viscosity versus ($1000/T$) for five binary mixtures: 0.6(**FF**), 0.6(**FH**), 0.8(**FH**), 0.6(**HH**) and 0.8(**HH**).

The temperature dependence of η is fitted with the following expression [42]

$$\eta = \eta_0 \exp\left(\frac{E_a}{k_\beta T}\right) \quad (8.2)$$

where k_β is the Boltzmann constant and E_a is the activation energy of the molecular rotation on the cone when the applied electric field is reversed. The Arrhenius plot of effective torsional viscosity for five binary mixtures is plotted in Figure 8.6. Far from the SmC* to SmA phase transition, a linear behavior is observed and from the slopes of the straight line the activation energy values in the SmC* phase (Figure 8.6) have been calculated and are listed in Table 8.3. For mixture with mole fraction $x_{\text{FH}}=0.409$, the SmC* range is too short to determine the activation energy. The values of the activation energy are within 0.18-0.28eV, as expected [42].

Table 8.3 Activation energy for five binary mixtures.

Mole fraction of mixture	Activation energy (eV)
$x_{FF} = 0.597$	0.28
$x_{FH} = 0.598$	0.23
$x_{FH} = 0.836$	0.18
$x_{HH} = 0.603$	0.21
$x_{HH} = 0.805$	0.20

8.7 Anchoring energy strength co-efficient measurement

The dispersion anchoring strength coefficient (W_D) and polarization anchoring strength coefficient (W_P) as a function of reduced temperature have been presented in Figures 8.7 and 8.8 respectively. The anchoring induces ferroelectric ordering close to the cell surfaces due to the polar and non-polar interactions of the molecules with aligning layer of the cell surfaces. The anchoring energy coefficient yields a quantitative characterization of the aligning liquid crystal molecules and corresponds to two different anchoring energy (i) the dispersion anchoring energy and (ii) polarization anchoring energy [20-23].

Dispersion anchoring energy arises from the non electrostatic interaction between the surface and liquid crystal molecules whereas the polarizing anchoring energy originates from the electrostatic force between the dipole moment of the superficial layers of the surface and liquids crystal molecules [20-23]. The temperature dependence of the dispersion anchoring strength coefficient (W_D) and polarization anchoring strength coefficient (W_P) is due to the increase in enthalpy of the molecule with temperature which ultimately break their interaction barrier [43]. The value of W_P and W_D is low for these binary mixtures which possess low P_s and low viscosity.

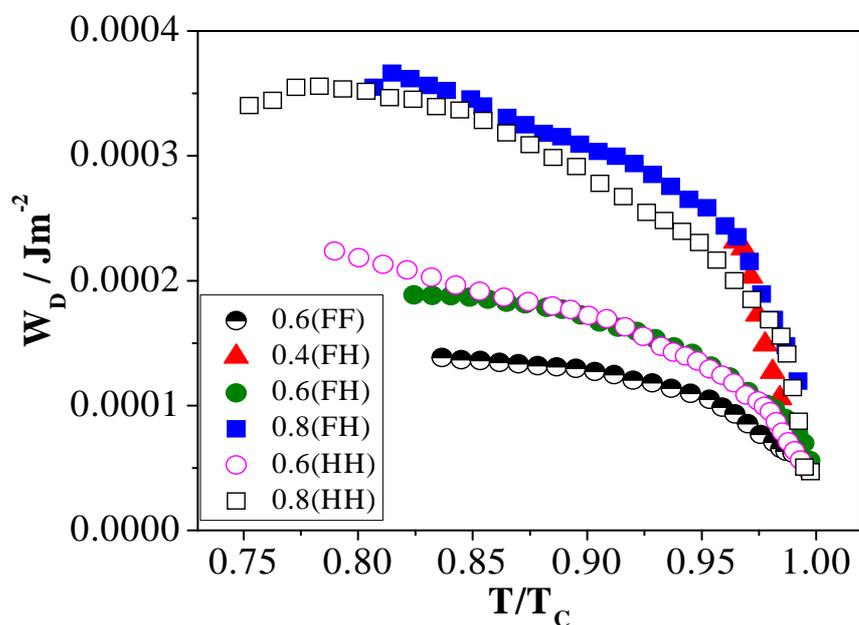


Figure 8.7 Dispersion anchoring strength coefficient (W_D) as a function of reduced temperature for six binary mixtures: 0.6(FF), 0.4(FH), 0.6(FH), 0.8(FH), 0.6(HH) and 0.8(HH).

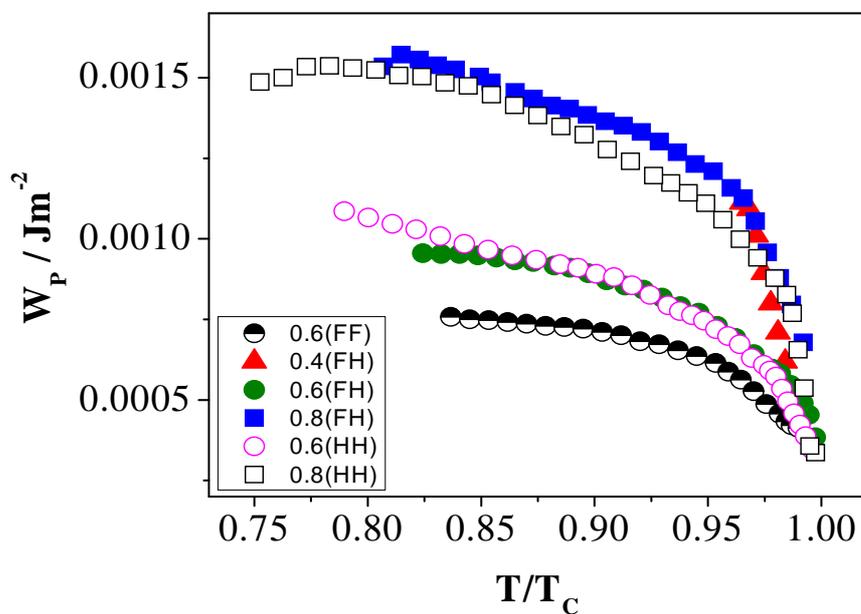


Figure 8.8 Polarization anchoring strength coefficient (W_P) as a function of reduced temperature for six binary mixtures: 0.6(FF), 0.4(FH), 0.6(FH), 0.8(FH), 0.6(HH) and 0.8(HH).

As shown in Figure 8.7, near the SmA-SmC* phase transition for all the six FLC mixtures reported here, it is observed that the values of W_D are linearly proportional to (T/T_C) . This observation has also been reported by others [20]. The values of W_P are higher than that of W_D , due to presence of polar fluorinated chiral esters and heterocyclic nitrogen atom in achiral PhP.

8.8 Conclusion

In this chapter the results based on the electro-optic studies of three binary systems, consisting of an achiral low viscous compound **PhP** with three different orthoconic antiferroelectric liquid crystals have been presented. For a more quantitative consideration of the differences in spontaneous polarization, relaxation time, effective torsional viscosity and effective anchoring energy coefficients, these values at a particular reduced temperature ($T/T_C=0.97$) for all the binary mixtures studied here, have been listed in Table 8.4.

Table 8.4 A comparative study of the physical parameters of the investigated six mixtures and their pure chiral compounds at $T/T_C=0.97$.

Mole fraction of mixtures	P_s (nCcm ⁻²)	τ (μ s)	γ (mPas)	W_D ($\times 10^{-4}$ Jm ⁻²)	W_P ($\times 10^{-4}$ Jm ⁻²)
$x_{HH} = 1.0$	173	37	257	85	126
$x_{HH} = 0.805$	6.5	29	8	2	9
$x_{HH} = 0.603$	3.8	19	3	1	6
$x_{FH} = 1.0$	155	28	171	76	77
$x_{FH} = 0.836$	7.6	30	9	2	10
$x_{FH} = 0.598$	3.9	16	2	1	6
$x_{FH} = 0.409$	7.1	37	13	2	10
$x_{FF} = 1.0$	153	205	171	49	103
$x_{FF} = 0.597$	3.0	13	2	0.8	5

It is of interest to note that the values of P_s reduce with increasing proportion of achiral **PhP** due to less chiral perturbation exerted by the chiral molecule via core-core interactions. This may be improved by introducing chiral components with multi-chiral centre in place of a single chiral centre. Reducing the P_s may elongate the helix *i.e.* the helical structure is distorted and the system become 'softer'.

The chiral orthoconic compounds induce a nonzero polarization in a non-chiral smectic C host. The polarity derived from the electron-withdrawing effect of nitrogen atoms in the rigid core of phenyl pyrimidine compound has a strong influence on the mesophase sequences. Such polar ordering interacts with the polar fluorinated ester compounds via transverse dipole-dipole coupling and/or chiral conformational interactions [28]. These interactions could, in turn, result in a significant asymmetric distortion of the smectic C lattice that further perturbs the orientational ordering of the atropisomeric core, *i.e.*, a synergistic effect. As a result these mixtures has emerged as very fast switching LC mixtures operating at room temperature and are convenient for passive addressing scheme at high multiplexing level and video rate with excellent contrast. Additionally, the structure property correlation presented for these binary systems indicate that fluorination of the aromatic ring has significant effect on the phase behaviour and physical properties of these materials. Potential applications of these mixtures for light shutter, photonics, telecommunication and high speed micro-display are foreseeable where a broad temperature range, low polarization and long pitch are desired [44,45].

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