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# Effect of Hydrogen Bond on Mesomorphic Phases of Binary Liquid Crystal Complexes

S Sundaram[1], G. Gowrishankar[2], Suganya B, Tony Diwahar, A

[1]*Centre for Materials Research, Department of Physics, Nehru Institute of Technology, Coimbatore-641 105, Tamil Nadu, India*

[2]*Department of Physics, Condensed Matter Research Laboratory (CMRL), Bannari Amman Institute of Technology, Sathyamangalam-638 401, Tamil Nadu, India*

[#] Corresponding Author email ID : vnvphysics@gmail.com; Phone:+91 9488021151, Fax +91 4295 226303.

**Abstract**

Hydrogen Bonded Liquid Crystalline (HBLC) complexes are synthesized from binary mixtures (different Wt%) of 4-decyloxy benzoic acid (10BAO) and cholesteryl acetate (CHA). Fourier Transform Infrared Spectroscopy (FTIR) studies confirm that the formation of intermolecular hydrogen bond in the binary complex. HBLC complexes are exhibiting the nematic phase along with tilted smectic phases. Phase transition properties of HBLC complexes have been investigated by means of Differential Scanning Calorimetry (DSC). The noteworthy observation is that there is a significant reduction of mesomorphic phases while decreasing Wt% of 10BAO combination with CHA and from the experimental observations, quenching of smectic C while decreasing Wt% is identified. Also enhanced phase width and lowering melting temperature in the HBLC binary complex is also noticed.

**Keywords**: HBLC complex, Nematic phase, DSC, Phase transition properties.

## INTRODUCTION

In recent years, there has been considerable quantity of research conducted with respect to the properties of binary liquid crystalline materials [1, 2]. Liquid crystals (LC) are truly attractive materials in terms of their properties for the fundamental understanding of molecular self-assembly and their remarkable success in commercial applications [3]. The formation of hydrogen bond (H-bond) through the non covalent interactions of molecules is a potential tool for self assembling the molecules to form the liquid crystal complexes [5]. Cholesteric liquid crystals combination with other mesogens, and their helical assembly of nematics, cover a wide range of potential applications in displays, polarisers, organic pigments, thermography and photonic devices [6-8]. The thermal and mesophase behaviour of binary mixtures formed from hydrogen-bonded nematic liquid crystals reveal that the nematic ranges of the produced mixtures are influenced by the mixture ratio and the difference in the alkyloxy chain lengths [9-12].

## MATERIALS AND METHODS

The liquid crystal compound of 4-decyloxy benzoic acid (10BAO) and cholesteryl acetate (CHA) were supplied by Sigma Aldrich, Germany and all the solvents used were E.Merk grade. The LC cell is placed in a hot stage MHCS400 (MicrOptik) where the temperature is monitored by a MTDC600 temperature controller (MicrOptik).Polarizing Optical Microscope (POM) has been used to observe the mesophases. Optical images of mesogens are captured using a Sony CCD.17.UH310 USB CCD 3.1MP camera during heating and cooling runs at the rate of $1^{o}C\ min^{-1}$ and the corresponding textures are analyzed by software. Shimadzu DSC60 Plus with Ta60 software (version 2.21) and TAC-60i mechanical auto-cooling system is used for obtaining transition temperatures and enthalpy values of mesogens. The samples are cooled at a rate of $10^{o}Cmin^{-1}$ to 35°C followed by a heating scan at a rate of $10^{o}Cmin^{-1}$ to a temperature above the expected clearing temperature. FTIR spectra are recorded (ABB FTIR MB3000) by making pellet of the mesogens analyzed them using the MB3000 software to identify the formation of H-bond in the complex.

The binary complex is designed and synthesized by adding one mole of CHA and different Wt% of 10BAO in N,N-Dimethyl formamide (DMF). The different Wt% HBLC are (CHA-1%+10BAO-0.125%),(CHA-1%+10BAO-0.25%), (CHA-1%+10BAO-0.50%) and (CHA-1%+10BAO-1%) represented as A, B, C and D.

## RESULTS AND DISCUSSION

The mesogenic phases and its textures have been experimentally examined using POM. The transition temperature for its corresponding phases has been given in table 1.There is an appearance of sharp peak at $1682cm^{-1}$ which clearly suggests the dimer formation, in particular the carbonyl group vibration. The presence of H-bond in the present complex is further inferred by the appearance of strong band shows the carboxylic acid group ν (O---H) at $2931cm^{-1}$ and the same is not observed in the pure CHA and 10BAO mesogens.

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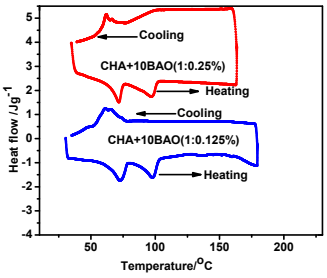


**FIGURE 1**. DSC thermogram of A and B HBLC Complex.

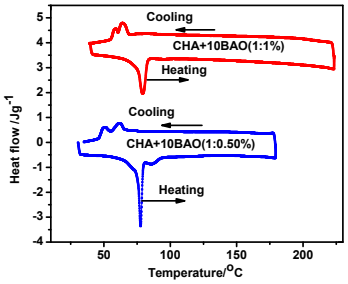


**FIGURE 2**. DSC thermogram of C and D HBLC complex.

The general phase sequences of the HBLC complexes with different Wt% are observed as,

**Iso. ⇄ Sm G ⇄ Crystal (A)**
**Iso. ⇄ Sm C ← Sm G ← Crystal (B)**
**Iso. ← N ⇄ SmC ← Sm G ← Crystal (C)**
**Iso. ⇄ N ⇄ Sm C ← Sm G ← Crystal (D)**

## DSC Studies

The DSC thermograms are obtained with scan rate of 10°C/min while heating and cooling cycles of A, B (Fig. 1) and C, D (Fig. 2) HBLC mixtures. The respective equilibrium transition temperatures corresponding to the enthalpy values of mesogens are listed in Table 1.The extended phase width (thermal span) 75.5°C in the nematic region, 36.8°C in Sm C and 4.3°C in Sm G is noticed. This observation clearly shows that the stabilization of phases is due to the formation of intermolecular hydrogen bond between the mesogens which creates a lath-like structure and the systematic reorientation of molecules themselves in the complex. Similarly, the wt% in the mesogen of 10BAO decreases; the mesogenic phases are also quenched.

**TABLE 1** Phase transition temperatures and enthalpy values of CHA + 10BAO HBLC obtained by various techniques.

| Compound | Phase | Technique | Cycle | Unit | Crystal - Melt | N | Sm C | Sm G | Crystal |
|---|---|---|---|---|---|---|---|---|---|
| CHA+10BAO 1 : 0.125% | G | POM | Heating | °C | 73.8 | @ | @ | 98.3 | |
| | | | Cooling | | | @ | @ | 73.2 | 65.9 |
| | G | DSC | Heating | °C (J/g) | 72.61 (21.8) | @ | @ | 97.8 (21.28) | 64.2 |
| | | | Cooling | °C (J/g) | | @ | @ | 72.6 (*) | 63.9 (18.83) |
| | | | | | | | | | |
| CHA+10BAO 1 : 0.25% | CG | POM | Heating | °C | 77.5 | @ | 93.4 | # | |
| | | | Cooling | | | @ | 93.1 | 68.9 | 61.3 |
| | CG | DSC | Heating | °C (J/g) | 67.8 (7.40) | @ | 92.9 (2.15) | # | |
| | | | Cooling | °C (J/g) | | @ | 92.8 (0.79) | 67.8 (*) | 60.6 (8.05) |
| | | | | | | | | | |
| CHA+10BAO 1 : 0.5% | NCG | POM | Heating | °C | 78.7 | # | 86.1 | # | |
| | | | Cooling | | | | 67.2 | 56 | 46.1 |
| | | DSC | Heating | °C (J/g) | 77.6 (24.07) | # | 85.7 (2.40) | # | |
| | | | Cooling | °C (J/g) | | 142.0 (0.57) | 66.3 (5.27) | 55.4 (*) | 45.7 (2.27) |
| | | | | | | | | | |
| CHA+10BAO 1 : 1 | NCG | POM | Heating | °C | 79.7 | 174.9 | 100.1 | # | |
| | | | Cooling | | | 177.0 | 101.4 | 64.6 | 61.3 |
| | | DSC | Heating | °C (J/g) | 80.1 (73.2) | 175.6 (3.8) | 100.5 (2.0) | # | |
| | | | Cooling | °C (J/g) | | 176.7 (0.1) | 101.2 (0.4) | 64.4 (1.8) | 60.1 (8.8) |

@ Not resolved * Merged with crystal # Monotropic

Another noticeable observation is that the melting point of the all HBLC complexes (A, B, C &D) is less than that of its pure mesogens in the complex and also considerably decrement of crystallization temperature, melting point and much lower enthalpy values are observed while compared to pure mesogens. The mixture of two liquid crystal compounds offers the much larger temperature range that exhibits the nematic phase for LCD applications.

## CONCLUSIONS

Thermal and optical characteristics of the binary mixture (different Wt%) of HBLCs have been studied. This molecular design strategy gave a fabulous method to modulate the phase behavior and transition temperatures of HBLC mesogenic complex. Abundant reduction of mesophases in HBLC complex is noticed while decreasing Wt% of mesogens. It can be observed that the combination in the LC mixture alters the thermal stability of the phases with respect to their thermal span. These studies may be a more useful to select suitable HBLC material for optical devices such as optical (light) modulator, memory and shuttering devices.

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