



SMART MATERIALS

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Abstract - *Liquid crystal has unique properties both isotropic liquid nature and anisotropic solid nature. It has sensitivity towards changes in temperature, concentration, pressure and presence of electric and magnetic fields. The liquid crystals exhibit the property of birefringence when they are subjected to crossed polarizer's under the polarizing optical microscope. They exhibit different textures at different temperatures as the molecules behave differently at each phase. such liquid crystals are called thermo tropic liquid crystals. Phase transition temperatures are significant for application point of view and can be determined through several techniques. Liquid crystals compounds exhibit non- covalent interaction between the molecules. These interactions include hydrogen bonding, metal co-ordination, vanderwall forces, electrostatic forces, etc. Hydrogen bonding focused great many features such as the rates of dynamic equilibrium, new phases and their thermal stability with low bond activation energies having wide applications in electro-optic displays, photo voltaic cells, fiber communication and fluorescent films etc. A comparative study of some liquid crystals using vibrational spectroscopy establishes hydrogen bond formation.*

KEYWORDS: *Liquid crystals, polarization, fiber communication, hydrogen bond.*

1. INTRODUCTION:

Aromatic carboxylic acids are the first compounds that exhibit Liquid Crystal (L.C.) nature due to hydrogen bond formation. A L.C. material synthesized with the help of hydrogen bond formation is called supra molecular liquid crystal. We can synthesize L.C. with intermolecular hydrogen bonding between a L.C. and non L.C. or between two L.C. or between two non L.C. materials which have great viability in applications.[1,2] synthesizing various liquid crystal complexes from the mixtures of mesogenic-mesogenic materials, mesogenic or non-mesogenic material and non-mesogenic nonmesogenic materials in different molecular ratios is a very active and vibrating area of the liquid crystal science[3-12]. In such complexes, the molecules of the compounds which involve the non covalent and covalent interactions follow the process of self-organization [13, 14] and possess special shapes and structures.[15-24].In the self-organized systems. Binary mixtures of hydrogen-bonded liquid crystals are of great importance due to their low bond activation energies[15, 25-34] and possible application in different electro-optic displays, photovoltaic cells, fibre communications, biological systems,[8,9] fluorescent films, etc., and these systems also widen the applicability of organic materials.[10] Furthermore, the hydrogen-bonded systems have a striking influence on

physical properties such as melting and clearing temperatures, [32] enthalpies, entropies, [10] quenching of phases, and inducing new phases with the wide thermal span[17]. In this paper, a novel homologous series of mesogenic materials is prepared through the development of hydrogen bond between COOH of mesogenic compounds p-n-alkylbenzoic acids (nBAs) where n=7-9 (nBA) and OH of non-mesogenic compound dodecyl- p-hydroxybenzoate (10HB). This chemical bond spreads over the molecular frame through the non-covalent intermolecular interaction between a proton acceptor (OH) of chemical moiety and a proton donor (COOH) moiety. This non-covalent intermolecular interaction induces and stabilizes the liquid crystalline phase in resultant homologues series liquid crystal complexes. Here, the OH of the DDHB moiety acts as a proton acceptor and COOH of nBA with different alkyl chain lengths (n=7-9) is known to be the proton donor for the self-organized hydrogen-bonded systems. A systematic investigation on physical parameters of the systems such as thermal and phase behaviour of the complexes are studied using polarizing optical microscope (POM), differential scanning calorimetry (D.S.C.) and spectroscopy.

2. EXPERIMENTAL

The chemical ingredients nBAs with 99% purity and DDHB & OBCA were procured from Frinton



Laboratory, New Jersey, USA. Infrared (IR) spectra of the compounds were recorded on an Alpha model BRUKER Infrared spectrometer (BRUKER Corporation, Billerica, MA, USA). Transition temperatures and enthalpies associated with liquid crystal phase transitions are determined by DSC performed on a DSCQ20 V24.2 Build 107 Universal V4.5 TA instruments under nitrogen atmosphere at the heating / cooling rate of 5°C/min. A small quantity of sample is placed on a commercially available glass slide which will usually keep in the hot stage of the POM (Meopta DRU3 Model; Meopta global manufacturers, Hauppauge, NY, USA) to observe the textures of the samples. The accuracy of the temperature measurements is $\pm 0.1^\circ\text{C}$. Canon EOS Digital REBELXS/EOS1000D (Canon Inc., Taiwan, China) is a digital single lens reflex camera with a 10.10 megapixel image sensors used to record the texture images of the sample through the crossed polarisers of the POM.

3. PREPARATION OF nBA: DDHB & nBA: OBCA (WHERE n=7-9) COMPLEXES

Homologous series of nBAs (where n=7-9) and DDHB & OBCA are obtained from Frinton Laboratories. nBA and DDHB are white crystalline compounds at room temperature. Hydrogen-bonded liquid crystalline complexes, namely, nBA:DDHB (where n=7-9) are prepared by the following procedure given. Required amount of samples for synthesis is weighed on a single pan electronic balance Dhona make, ER-180A (Kolkata, West Bengal, India) with an accuracy of 0.01mg. Equimolar (1:1) ratio of nBA and DDHB is used for the preparation of liquid crystal complexes, 7BA:DDHB, 9BA:DDHB. Compounds are taken individually and mixed in the pyridine solvent (20 ml). Thus, the naturally existing dimeric forms of nBA compounds with complementary hydrogen bond are converted into the monomeric forms. Now, the two solutions are mixed and kept under constant stirring at 80°C for 4 hrs. Then most of the pyridine is removed by vacuum distillation process. It means the resultant homogeneous mixture was reduced to almost dryness by removing the excess pyridine under a controlled vacuum filtration. The white crystalline product was dried and re-crystallized from dichloro-methane solution. The yielding is about 85%.

The present work deals with the comparison of two L.C. complexes one with a combination of two L.C. materials p-n-alkyl benzoic acid and p-octyloxy benzylidene cyano aniline (nBA:OBCA) and the other is with one L.C. and non L.C p-n Alkyl benzoic acid and dodecyl hydroxy benzoate (nBA:DDHB.) where n=7&9. In both the cases the

compounds are monotropic showing smectic phase only in cooling cycles. In heating cycle from solid they become directly Isotropic without exhibiting any L.C. phase, quenching nematic phase in the pure compounds of nBA. But in case of nBA:DDHB, while cooling transition takes place at lower temperature. These compounds are monotropic exhibit smectic G phase. The growth in inducement of smectic A phase with increase in alkyl chain length shows the influence of the non polar tails on the rigid cores that is the semiflexible tail chains cause enough disorder and keep the cores to obtain partial positional order from isotropic phase which leads to SmA phase in nBA:OBCA. The donors with larger enthalpy required for orientation along director due to its rigid nature with flexible ends allowed for self assembling due to non-covalent interaction. This is the reason for reduced transition temperature, broadened thermal span decreased enthalpy and entropy quenching nematic phase of donors. The phase transition temperature observed through thermal microscopy is in reasonable agreement with those in the D.S.C thermograms. A detailed IR spectral investigation in solid suggests that the acid and phenol groups acts as both proton donor and proton acceptor respectively. The infrared spectroscopy frequencies of nBA:DDHB show the presence of a strong intense bond due to C=O mode of benzoic acid moiety at 1681.24 cm^{-1} . This strongly supports the existence of 9BA moiety in a monomeric form upon complexation. Further the infrared spectral studies are convinced with respective functional groups of donor at 1681.24 cm^{-1} , 1277.57 cm^{-1} and 3385.79 cm^{-1} of C-O and OH and acceptor with its in plane bend IPB, out plane bend OPB at 1277.57 cm^{-1} 639.21 cm^{-1} of C-O in their respective regions. In case of nBA:OBCA from FTIR and polarizing optical microscopy (POM) investigation, it is concluded that the hydrogen bond is formed between O-H group of p-n-alkyl benzoic acid and the CN group of OBCA. The intermolecular H-bonding interactions between the terminal functional groups of the molecule (O-H) and CN influence their molecular packing that is the molecules of benzoic acid is regularly arranged head-to-tail with adjacent molecule CN in the same layers.

4. CONCLUSION

The complexes with odd alkyl carbon numbers show wide liquid crystalline range. This shows the influence of the alkyl carbon number on the intermolecular H-bonding. Diagrams of D.S.C and FTIR of 7BA:DDHB & 9BA:DDHB and BA:OBCA and 9BA:OBCA.

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