ABSTRACT

Liquid Crystals (LCs) present an interesting and fascinating state of soft condensed matter whose self-organizing properties have propelled huge research interest both from fundamental as well as technological points of view in the modern era. LCs or mesophases are intermediate state existing between the isotropic liquid and the crystalline solid. The variety of mesophases provide a good platform to study the nature and properties of different phases. Their uses in display technology put them commercially high valuable. Fundamental mesogenic behaviour of liquid crystalline compounds is strongly affected by the molecular structure and organization of mesophases. It is very significant to study the behaviour of phase transitions as well as the physical properties of different liquid crystalline compounds and their binary mesogenic mixtures in order to characterize the materials.

In this thesis eight chapters have been discussed including introduction (Chapter-1), experimental and theoretical background (Chapter-2) and ending with the concluding remarks (Chapter-9). Among six main chapters (Chapters: 3-8), first four chapters have been entirely devoted to the study of phase transitions and the associated critical phenomena in order to achieve the idea about the nature of the different mesophase transitions related to the investigated materials (achiral as well as chiral compounds) and their binary mixtures.

The main focus has been made on the variation of the critical behaviour of the phase transitions with the change of mesophase range by preparing suitable liquid crystalline bi-component mixtures (Chapters-3,4,5,6). The rest two chapters mainly concern with the electro-optic and dielectric properties of some pure chiral ferroelectric liquid crystalline (FLC) compounds and their binary mixtures (Chapters-7,8).

Chapter-1: This chapter has given some introductory ideas about the liquid crystals and their classification as well as the existing phases associated with the liquid crystalline compounds related to the work of this thesis.

Chapter-2: This chapter describes an overview of a few existing theories corresponding to different liquid crystalline (LC) mesophases, their transitions and related to different physical properties. The experimental procedures employed to quantify various physical properties of different LC compounds and mesogenic binary mixtures have also been discussed.

Chapter-3: In the field of liquid crystalline research the isotropic to nematic (I-N) phase transition has frequently been studied. In spite of numerous data available about the critical behaviour of this transition for pure compounds, the systematic study on mixed systems are scanty in the literature. Further, innumerable studies have been performed during the last few decades in order to determine the nature of the nematic to smectic-A (N-SmA) phase transition. Yet it is open for further studies. In this chapter

- The phase diagram, critical behaviour and order character of the I-N and the N-SmA phase transitions of two polar-polar binary systems (i) 4-n-heptyloxy-4′-cyanobiphenyl (7OCB) and 4-n-octyloxy-4′-cyanobiphenyl (8OCB); (ii) 4-n-octyloxy-4′-cyanobiphenyl(8OCB) and 4-n-nonyloxy-4′-cyanobiphenyl (9OCB) have been discussed by means of a high-resolution birefringence (Δn) measurement. By preparing these two binary systems one can be able to get a wide variation of the nematic range.
- The value of the order parameter critical exponent β, obtained from four parameter fitting, clearly indicates the weakly first order nature of the I-N phase transition *i.e.*, the so called tricritical hypothesis at which β = 0.25 has been established.
- The renormalization group expression has been adopted to extract the critical exponent (α') obtained from the birefringence data which is similar to the specific heat capacity critical exponent (α). The α' for the N-SmA phase transition indicates a uniform crossover behaviour and has appeared to be non-universal in nature. With increasing concentration of the higher homologues for both the binary systems, the said transition reveals a strong tendency to be driven towards the tricritical nature.
- A co-relation between the critical exponent (α') and the McMillan ratio (T_{NA}/T_{IN}) has been established from this work. Furthermore, the critical exponent (β') has been extracted from fitting of the Δn data below the N-SmA phase transition and the value of the susceptibility critical exponent (γ') has been evaluated by using Rushbrooke equality. These critical exponents (β' and γ') are also found to support the crossover behaviour as put forward by the α' variation with the McMillan ratio.

Chapter-4: Re-entrance of phases is one of the most unusual behaviour of liquid crystalline systems where a phase of lower order appears below a phase of higher order at low temperatures. In the literature, the occurrence of two tricritical points one for the N-SmA and the other for the smectic-A to re-entrant nematic (SmA-N_R) phase transitions have been predicted on the basis of both thermodynamic analysis as well as phenomenological theories. However, the existence of the SmA-N_R tricritical point has not been experimentally verified. So, it is very interesting to select a suitable system for a careful high-resolution optical study near the SmA-N_R phase transition. In this chapter

- Two pure compounds 4-n-hexyloxy-4′-cyanobiphenyl (6OCB) and 4-n-octyloxy-4′-cyanobiphenyl (8OCB) has been chosen to prepare the binary mixtures for investigation of the SmA-N_R phase transition with the aid of optical transmission method.
- This work provides the experimental evidence of the existence of two tricritical points (TCP) one corresponds to the N-SmA phase transition and other corresponds to the SmA-N_R phase transition of the binary system 6OCB+8OCB. For the first time, this result conclusively shows the critical nature of the SmA-N_R phase transition experimentally.

The ferroelectric and antiferroelectric liquid crystals have become a subject of most intense area in the field of liquid crystalline research, since their discovery. The extraordinary optical and electro-optical properties of these novel phases make them potentially of high demandable in the flat panel display applications both in ferroelectric and antiferroelectric display

devices (FLCDs and AFLCDs). So far, numerous studies have been performed involving various phase transitions associated with the liquid crystalline compounds composed of achiral molecules, but the experimental studies involving the behaviour of mesophase transitions related to the LC compounds made up of chiral molecules have quite limited in the literature. It has been established that, the thermal as well as the optical investigations are very powerful tools which provide the significant information on critical fluctuations in the vicinity of the phase transitions. For this purpose, Chapter-5 and Chapter-6 have been devoted to investigate the critical behaviour in the vicinity of the phase transitions corresponding to the chiral antiferroelectric as well as ferroelectric liquid crystalline compounds.

Chapter-5: This chapter describes detailed analysis of the nature of phase transitions among chiral smectic phases associated with the two enantiomers of the antiferroelectric liquid crystalline compound 4-(1-methyl heptyloxycarbonyl) phenyl 4′-octyloxybiphenyl-4-carboxylate (MHPOBC) and their racemic mixture by means of high-resolution birefringence data obtained from optical transmission method (OT) and the specific heat capacity measurement by using modulated differential scanning calorimetry (MDSC) method. The critical exponent (α) from the specific heat capacity anomaly $\Delta C_P(T)$ and the critical exponent (α') from the differential quotient $Q(T)$ of the birefringence (Δn) have been extracted in order to

- Investigate the isotropic to smectic-A* (I-SmA*), smectic-A* to smectic-C$_\alpha^*$ (SmA*-SmC$_\alpha^*$) phase transitions in both the enantiomers of MHPOBC. A comparison of heat-capacity critical exponent found from

the mean-square fluctuations of the tilt angle $\langle \delta\theta^2(T) \rangle$ and the critical exponent (α') explored from the birefringence differential quotient $Q(T)$ for the SmA^*-SmC_α^* phase transition has also been done for both pure R-MHPOBC and S-MHPOBC. The critical exponents obtained using two different techniques agrees excellent well and indicates weakly first order nature of the I-SmA^* phase transition and 2nd order nature of the SmA^*-SmC_α^* phase transition.

- Detailed study about the nature of the phase transitions associated with the tilted SmC^* sub-phases in both the materials R-MHPOBC and S-MHPOBC.
- Study of the pretransitional behaviour and the phase transitions involved in the racemic mixture of the antiferroelectric compound MHPOBC.

Chapter-6: In this research field, it is also very important to observe the phase behaviour of chiral analogue of the SmA-SmC and N-SmC phase transitions. The main theme of this chapter are as follows

- This chapter emphasizes on high-resolution birefringence and heat capacity measurements to test the possibility of crossover behaviour from 3D-XY to tricritical nature of the SmA^*-SmC^* phase transition with the reduction of the SmA^* temperature range by preparing the suitable binary mixtures composed of the chiral ferroelectric liquid crystals (FLCs) **E8/7** and **E10/10** synthesized from the (S)-lactic acid derivatives. Due to the very sensitive nature of light about the average molecular direction, the optical transmission method gives very precise data in the near vicinity of the transition and successfully detect the true critical region belonging to the transition.

- The spontaneous polarization of all the investigated pure components as well as their binary mixtures have been determined. The variation of the extracted critical exponents (α, α') with the saturation value of the spontaneous polarization have also been examined in order to get a preliminary idea about the crucial factors that drive the SmA^*-SmC^* phase transition from second order towards the first order nature.

In certain applications the design of LC materials with ferroelectric orderings still remains a crucial challenge, which needs fundamental knowledge about the relevant relationships between molecular structure with mesomorphic and physical properties as well as their impact on the mechanisms of the phase transitions. In this context, Chapter-7 and Chapter-8 have been introduced.

Chapter-7: This chapter mainly concerns with the study of the self-assembling behaviour of several lactic acid derivatives with some ester linkage groups in the molecular core.

- The molecular structure-physical property correlations have been discussed in the light of the spontaneous polarization (P_S), response time (τ) and torsional viscosity (η) for eight pure chiral ferroelectric liquid crystalline (FLC) compounds. The activation energies of all the investigated chiral FLC compounds have also been determined from the best fitted Arrhenius plot of the torsional viscosity.
- The dielectric investigations allow one, to understand the molecular dynamics of the materials. The temperature dependence of static dielectric permittivity (ε), dielectric anisotropy $(\Delta\varepsilon)$ and the dielectric

spectroscopic studies are also very significant part of this chapter. All the investigated pure compounds show negative dielectric anisotropy. It is necessary to highlight that LC materials with negative dielectric anisotropy can be very desirable for use in construction of direct-view and projection LC displays. The tilted ferroelectric SmC^* phase has been studied by broad band dielectric spectroscopy and the results reveal a strong Goldstone mode in the ferroelectric SmC^* phase with ~ kHz relaxation frequency.

Chapter-8: No single material can exhibit all the desired properties for different applications. In order to fulfil all the requirements of the device manufacturer, preparation of suitable binary mixtures is one of the most simple and elegant way in the field of LC research. Keeping this in mind some bi-component mixtures have been prepared by using pure chiral FLC compounds and Chapter-8 has been introduced for this purpose, in which

- Investigations of these chiral FLC binary mixtures in the light of the static dielectric permittivity (ε), dielectric anisotropy $(\Delta\varepsilon)$, spontaneous polarization (P_S), response time (τ), torsional viscosity (η) and dielectric spectroscopy have been done.
- The most highlighted finding is that, the response time can be varied from 9 μs to 47μs by preparing binary mixtures of the two investigated systems. Such low values of response time may become very useful for fast electro-optical switching devices. This chapter mainly contributes to the preparation and investigation of some smart multifunctional FLC mixtures for better tuning of the physical properties aimed for optoelectronic and photonic applications.

From the results of Chapter-7 and Chapter-8 it has been pointed out that, the presence of large spontaneous polarization, very low response time, low viscosity and quite large negative dielectric anisotropy in all the studied pure chiral ferroelectric liquid crystalline (FLC) compounds as well as their binary mixtures makes them as promising candidates for applications in photonic as well as for fast switching electro-optic devices.

Chapter-9: Finally, the thesis ending with this chapter, which has included all the concluding remarks taken from each chapter of the thesis.