Abstract

Investigations of phase transitions and critical phenomena in liquid crystals (LCs) are the focus of great attention in soft condensed matter research. The characteristic behavior of different mesophases impart a significant role in determining the phase transitional nature in liquid crystal system. Several extensive experimental attempts have been made so far to characterize a wide variety of phase transition in pure calamitic samples and binary mixtures of homologous compounds. Apart from the calamitic compounds, the divergent shaped bent-core liquid crystals exhibit a number of exotic mesomorphic behaviors and have been observed to influence the molecular interaction and hence the mesophase transitions in binary mixtures with calamitic compounds. This dissertation deals with systematic experimental investigations on the critical phenomena and phase transitional behavior of the isotropic–nematic (*I*–*N*), nematic–smectic-*A* (*N*–Sm-*A*) and smectic-*A*–smectic-*C* (Sm-*A*–Sm-*C*) phase transitions in binary mixtures comprising of calamitic and bent-core compounds. Additionally, investigation of different physical properties in some pure and binary liquid crystal systems has been measured to probe the molecular interactions in several mesophases. Concise overviews of the entire dissertation along with salient features of the outcome are described below.

Chapter 1 describes the basic concept of liquid crystal materials along with their classifications. The molecular arrangements and general behavior of different mesophases for both of the calamitic and bent-core liquid crystal systems have been discussed. Besides, a brief discussion about the phase transitions along with the critical phenomena and related critical exponents has been explored.

Chapter 2 provides the detailed description about different experimental setups and relevant investigation procedures employed to study different LC compounds and mesogenic binary mixtures. Additionally, the supporting

theories of various mesophase transitions related to this dissertation have been discussed.

Chapter 3 illustrates the effect of hockey stick-shaped mesogen 4-(3-decyloxyphenyliminomethyl)phenyl-4-decyloxycinnamate (SF7) on the critical behavior at the isotropic–nematic (*I*–*N*) and nematic–smectic-*A* (*N*–Sm-*A*) phase transitions in some binary mixtures with the calamitic 4′-octyloxy-4-cyanobiphenyl (8OCB), by analyzing the temperature dependent optical birefringence (Δn) data.

i. Introduction of the molecular bend of the angular mesogenic dopant significantly destabilizes the temperature range of the nematic phase of the calamitic compound.
ii. The extracted order parameter critical coefficient β related to the *I*–*N* phase transition has found to reveal a good conformity with the tricritical hypothesis for all of the studied mixtures.
iii. The obtained critical exponent (α', β') values describing the critical fluctuations at the *N*–Sm-*A* phase transition reveals a non-universal nature and demonstrates a strong dependency on the width of the nematic phase.
iv. Shrinkage of nematic phase range demonstrates a strong tendency to drive the *N*–Sm-*A* phase transition towards a first-order nature.

Chapter 4 includes the dielectric and visco-elastic properties of the binary system as discussed in chapter 3.

i. All the investigated mixtures possess a large positive dielectric anisotropy ($\Delta\varepsilon$), although a noticeable reduction has been found by increasing the diverse-shaped dopant concentration due to strong polar interaction of anti-parallel aligned dipoles.
ii. Investigation on the pretransitional phenomena in the vicinity of *I*–*N* phase transition suggesting a tricritical character for all the investigated mixtures.

iii. Parameterization of dielectric permittivity close to the *N*–Sm-*A* phase transition reveals a quite good consistency about the nature of the transition obtained from the high-resolution optical birefringence measurements for the present binary system.

iv. The splay elastic constant (K_{11}) and the rotational viscosity (γ_1) are found to exhibit a systematic temperature and concentration dependency along with the magnitude in between typical bent-core and calamitic compounds.

v. Effect of the induced molecular clusters within the mixtures successively deteriorates the nematic phase range and exhibit a crossover character from second order to first order in nature for the *N*–Sm-*A* phase transition.

In **Chapter 5,** investigation on critical behavior has been explored at the Sm-*A*–Sm-*C* phase transition of a homologous calamitic binary system (5-*n*-ethyloxy-2-(4-nonyloxy-phenyl)pyrimidine (PhP1) and 5-*n*-heptyloxy-2-(4-*n*-nonyloxy-phenyl)pyrimidine (PhP2) by studying the temperature dependent optical birefringence data. The *N*–Sm-*A* and *I*–*N* phase transitions have also been studied for the same binary system.

i. Analysis of Δn value in close vicinity of both the *N*–Sm-*A* and Sm-*A*–Sm-*C* phase transitions explored the difference between the order natures of these transitions that solely depends upon the temperature range of the *N* and Sm-*A* phases respectively.

ii. An approximate range of the Sm-*A* phase has found to be ~10.5 K to demonstrate a tricritical point of the Sm-*A*–Sm-*C* phase transition which is somewhat greater than that of the *N* phase range (~2.5 K) for the *N*–Sm-*A* phase transition.

iii. The transitional behavior of the Sm-*A*–Sm-*C* phase transition has found to be really critical over the range 3×10^{-3} and follows a unique curve against temperature ratio (T_{AC}/T_{NA}) in comparison to

the similar curve obtained for the *N*–Sm-*A* phase transition against McMillan ratio (T_{NA}/T_{IN}).

iv. The critical exponent (β), characterizing the critical anomaly at the *I–N* phase transition reveals a good consistency with the tricritical hypothesis.

Chapter 6 focuses on the extensive analysis of the critical behavior in the vicinity of Sm-*A*–Sm-*C* phase transition in some binary mixtures consisting of a hockey stick-shaped compound 4-(3-n-decyloxy-2-methyl-phenyliminomethyl) phenyl 4-n-dodecyloxy cinnamate (H-22.5) and a calamitic mesogen 4-cyano-4′-heptyloxybiphenyl (7OCB).

i. The yielded values of the effective critical exponent (α') have found to be non-universal in nature and exhibit a linear dependence against the Sm-*A* phase range.

ii. The values of α' follow the same curve in between 3D-*XY* and tricritical (TCP) limit as observed in previous work (chapter5).

iii. The present system characterizes a broad tricritical range for the Sm-*A*–Sm-*C* phase transition.

Chapter 7 deals with the study of the influence of an achiral hockey stick-shaped compound (H-22.5) on the optical, dielectric and electro-optical properties in some binary mixtures with chiral ferroelectric compound (S)-(+)-4′-(ω-alkanoyloxy)alkoxybiphenyl-4-yl-4-(1-methylheptyloxy)benzoates (2H6R).

i. Addition of hockey stick-shaped compound completely suppress the Sm-*C** phase of the pure chiral compound and induces two broad ranged frustrated TGB phases (TGBA and TGBC*) in between cholesteric (*N**) and Sm-B^*_{hex} phases for all of the investigated mixtures.

ii. The dielectric anisotropy ($\Delta\varepsilon$) value reveals an inversion from positive to negative and the temperature range of the positive

dielectric anisotropy region has found to increase by increasing the amount of H-22.5 mesogen.

iii. The temperature dependent spontaneous polarization (P_s) value in the TGBC* phase significantly decreases with increasing hockey stick-shaped molecular concentration, while the response time (τ) and effective torsional bulk viscosity (η) exhibit a higher value than that of the Sm-*C** phase of the pure compound.

iv. The investigation on the frequency-dependent dielectric spectroscopy demonstrates the signature of the soft and Goldstone modes in the *N** and TGBC* phases respectively. However, the intermediate TGBA phase represents a transition from soft mode in *N** phase to a Goldstone mode in TGBC* phase with a greater value of activation energy.

All the physical properties in those mixtures have been discussed by considering the perturbation introduced by the achiral hockey stick-shaped compound.

Chapter 8 is devoted to a comparative study of three pure homologous bent-core compounds (**1/7**, **1/9** and **1/10**) derived from 4-cyanoresorcinol bisbenzoates based on the dielectric spectroscopy and the electro-optical investigation.

i. Compounds **1/7** and **1/9**, exhibit a high-frequency molecular relaxation mode (P_1) and a low-frequency molecular mode (H_1) in the N_{CybC} phase of the planar (HG) and homeotroically (HT) aligned samples. Additionally another distinct high-frequency molecular mode (H_2) appears in HT cell for both the compounds which is further influenced by the effect of anti-ferroelectric ordering of molecular dipoles in adjacent layers of Sm-$C_{(I)}$ phase for compound **1/9**.

ii. The higher homologue (**1/10**) exhibits a longitudinal relaxation mode (H_2) and a transverse mode (P_1) throughout the mesmophic

region along with another relaxation mode (P_2) in planar aligned Sm-$C_{(I)}$ phase.

iii. The field reversal polarization technique and the simultaneous observation of optical textures in polarizing optical microscope confirm the polar nature of these mesophases.

These outcomes have been explained by considering the structural changes of the molecules by increasing the chain length and effect of their association in dielectric parameters.