ABSTRACT

This dissertation is mainly focused on different aspects of the critical behavior at the nematic-isotropic (N–I) and smectic A-nematic (SmA–N) phase transitions in a number of binary liquid crystalline systems by means of diverse experimental techniques. A comprehensive study of the phenomenon of induction of nematic and smectic A phases through the investigation of various physical properties has also been carried out. This thesis illuminates how the phase behavior of liquid crystalline systems plays a significant role in determining the nature of phase transitions involved.

The present work consists of nine different chapters describing a careful construction of complete phase diagram of some binary liquid crystalline systems with suitable concentrations and the measurement of the high resolution birefringence, refractive index, static dielectric permittivity, dielectric anisotropy, high resolution density, splay elastic constant and rotational viscosity of those mixtures. Studies have been carried out for different mixture concentration spanning the N-I, SmA-N and smectic A-isotropic (SmA-I) phase transitions. The outlines of the subsequent chapters of this thesis are described below.

Chapter 1 explores the basic ideas related to thermotropic liquid crystals and emergence of induced phases followed by a brief review about phase transition.

Chapter 2 illustrates various experimental techniques entailed in this work in conjunction with the essential theoretical backgrounds.

Chapter 3 is devoted to high resolution birefringence study in some mixtures of alkoxycyanobiphenyl (nOCB) and alkylcyanobiphenyl (nCB) liquid crystals.

- Near the SmA-N transition birefringence data exhibits a pretransitional behavior which is found to be enhanced with shortening of nematic range.
- The critical exponent α at SmA-N transition exhibits a crossover between the 3D-*XY* limit and tricritical point. The limiting value of McMillan ratio at which SmA-N transition changes its character from second order to first order is almost equal for all the three

binary systems ranging from 0.992 to 0.997 while for the 3D-*XY* limit the same varies from 0.937 to 0.942.

- The critical exponent α at N-I transition assumes a value of around 0.5 supporting a tricritical nature of the N-I transition, indicating a conformity with the outcomes of four parameter fit to birefringence, resulting β values close to the tricritical value (β=0.25).

Chapter 4 presents the emergence of induced nematic phase in a binary system comprising of 5-trans-n-pentyl-2-(4-isothiocyanatophenyl)-1,3-dioxane (5DBT) and 4-cyano-4′-n-decyloxy-biphenyl (10OCB).

- The ordinary and extraordinary refractive indices display normal temperature variation with a rapid change near N-I transition.
- This binary system shows existence of two tricritical points for SmA-N transition on either side of the phase diagram at x_{5DBT} = 0.123 and 0.894 with a common value of McMillan ratio 0.992.
- However, the 3D-*XY* limit for the SmA-N transition is reached almost exactly at x_{5DBT}=0.696 with $\alpha = -0.0068 \pm 0.0004$ for McMillan ratio 0.912.

Chapter 5 highlights on the static dielectric study of the induced nematic system 5DBT+10OCB.

- In SmA phase parallel component of dielectric permittivity shows a pronounced decrease for most of the mixtures due to dipole-dipole correlation.
- The effective molecular dipole moment (μ_{eff}) increases with increase in temperature while the angle of inclination (ω) remains almost invariable in low temperature region but increases somewhat near the clearing temperature (T_C).
- The isotropic dielectric permittivity (ε_{iso}) reveals a strong pretransitional behavior near T_C due to the strength of transition, correlation of dipole moments and formation of pseudo-nematic domains in the isotropic phase.

- Parameterization of dielectric permittivity by the fluid like model results a systematic concentration dependence of the discontinuity (ΔT^*) at the N-I transition.

Chapter 6 covers high resolution density studies for a polar-non polar binary system consisting of 4-heptyl-4′-*n*-cyanobiphenyl (7CB) and 4–n–pentyl–4′–n′–hexyloxybenzoate (ME6O.5) showing induced smectic A phase.

- The density value increases on lowering temperature representing a relatively higher packing of molecules within the mesophases.
- SmA-I transition possesses higher value of ΔT^* and meta-stable region near T_C than the same for N-I transition.
- Both the N-I and SmA–I transitions is accompanied by a decrease in the discontinuity ΔT^* with increasing concentration of the polar-compound 7CB.
- Like all other cases the critical exponent α for the N-I and SmA-I transitions has been found to accomplish the tricritical value 0.5 indicating the fluid like resemblance in the isotropic phase of the aforesaid transitions.
- This induced smectic system endows with two tricritical points (TCP) for the SmA-N transition located at $x_{7CB} = 0.232$ and 0.627 on both sides of phase diagram.

Chapter 7 summarizes a comprehensive study on the orientational order parameter ($\langle P_2 \rangle$) and its critical exponent (β) for a polar-polar binary system consists of 5-trans-n-butyl-2-(4-isothiocyanatophenyl)-1,3-dioxane (4DBT) and 4-cyano-4′-n-undecyloxy-biphenyl (11OCB).

- The N-I transition is distinguished by a sharp increase of $\langle P_2 \rangle$ followed by a gradual increase within the mesophase due to enhanced molecular ordering.
- The agreement between the experimental $\langle P_2 \rangle$ values from birefringence measurements with those calculated from mean-field theory has been found to be poor near T_C while far from T_C, $\langle P_2 \rangle$ can be well described by the theoretical values.

- The three-parameter Haller type fitting results comparatively lesser value of the exponent β, however the four-parameter fitting procedure to birefringence and dielectric anisotropy ($\Delta\varepsilon$) yields a consistent β values close to 0.25.

Chapter 8 contemplates a detailed investigation on the splay elastic constant (K_{11}) and rotational viscosity (γ_1) for the binary system 4DBT+11OCB.

- The K_{11} displays normal temperature dependence in the nematic phase for most of the concentrations except for x_{4DBT} = 0.787 and 0.884 exhibiting a stiffening of the same as the SmA phase attains.
- The relaxation time (τ_0) exemplifies an evident digression with increasing concentration of 4DBT in the range 0.393-0.707 due to the lesser inter-molecular packing of two mesogenic compounds with different core unit.
- In the vicinity of the SmA-N transition for some mixtures the stiffening of γ_1 is accounted with a critical exponent ν close to 0.33, signifying a deviation from the corresponding mean field exponent ($\nu = 0.5$).

Chapter 9 concludes the thesis with a summary of the main outcomes and implications for future scopes which could extend the work presented in this thesis.