CHAPTER 9

Conclusions

The dissertation entitled "*Phase transition in binary liquid crystalline mixtures*" submitted for the degree of Doctor of Philosophy (Physics) of the University of North Bengal is mainly focused on the critical behavior at the nematic-isotropic (N-I) and smectic A-nematic (SmA-N) phase transitions in some binary liquid crystalline systems using different experimental techniques. The aim of this dissertation is to provide a clear idea about the phase behavior as well as the nature of the phase transitions involved. The thesis comprises of eight chapters.

In the first chapter, a brief introduction to liquid crystals (LCs) has been given, particularly the thermotropic liquid crystals and different mesophases exhibited by LCs has also been pointed out. Necessity of mixture formulation of liquid crystalline compounds and appearance of the induced phase has been illustrated. Finally, a very concise review about the phase transition is also given in this chapter.

In chapter 2, different experimental techniques used in this work has been discussed elaborately and the relevant theoretical backgrounds are highlighted. These useful experimental techniques facilitate to characterize several physical properties of the liquid crystalline materials under study. The experimental techniques employed are phase detection by the texture studies, refractive index, optical birefringence, static dielectric permittivity, dipole moment, density, splay elastic constant and rotational viscosity measurements. The molecular statistical theory of Maier and Saupe for the nematic phase as well as nematic to isotropic

(N-I) phase transition is presented. The qualitative behavior of the smectic A phase or the SmA-N phase transition has also been discussed in the light of the McMillan model. Moreover, the phenomenological theory of phase transition in liquid crystals, the so called Landau-de Gennes theory has been dealt with in detail. First the basic ideas of Landau theory are explored. Then this theory is extended to the nematic-isotropic (N-I) as well as smectic A-nematic (SmA-N) phase transitions. Finally, some attention has also been paid to the elastic continuum theory and Freedericksz transition.

Chapter 3 deals with the phase diagram of three binary systems comprising of alkoxycyanobiphenyl (nOCB) and alkylcyanobiphenyl (nCB). These binary systems have been selected in such a manner that the nematic range may vary suitably with the concentration of the mixtures. The high resolution birefringence (Δn) data exhibits a clearly distinguishable pretransitional behavior within a temperature range of around 1-2K above and below the smectic A-nematic transition. This pretransitional signature is found to be enhanced with a reduction in nematic range in the studied mixtures. The birefringence data have been rather thriving in a precise probing of the transitional character at both the nematic-isotropic (N-I) as well as smectic A-nematic (SmA-N) phase transitions. At the SmA-N transition the diverging behavior of a differential parameter Q(T) has found to be well described by a simple power-law expression and the effective critical exponent (α) so obtained is strongly dependent on the nematic range. Reduction of the nematic range of the investigated mixtures drives the SmA-N transition from second order to first order nature due to the enhanced coupling between the nematic and smectic A order parameters. Indeed, the evolution of the critical exponent (α) with respect to the McMillan ratio (T_{SN}/T_{NI}) suggests that the key parameter is the nematic range which governs the order of the SmA-N phase transition. The α values are found to demonstrate a crossover behavior between the 3D-*XY* limit and tricritical point (TCP). The limiting value of the McMillan ratio at which the SmA-N transition changes its character from second order to first order is nearly 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. Furthermore, a precise study of the transmitted intensity in the isotropic phase of several

mixtures of the binary system 9OCB+7CB endows with a clearly distinguishable pretransitional behavior just above the clearing temperature (T_{NI}). This is due to some short of pre-nematic short range ordering, appearing in the vicinity of the N–I transition and their preferred alignment under the influence of strong surface anchoring in the thin sample of liquid crystals. The parameterization of this critical fluctuation as used for the SmA-N transition leads to a rather valuable quantization of the pretransitional aspects near the N-I phase transition. The critical exponent α at the N-I transition assumes a value of around 0.5 irrespective of the concentration supporting a tricritical nature of the N-I transition for all the studied mixtures. In addition, a four parameter fit model consistent with the weakly first order nature of the N-I transition results order parameter critical exponent β very close to the tricritical value ($\beta = 0.25$). This certainly implies an excellent conformity with the outcomes from the parameterization of the critical fluctuation of birefringence at the N-I transition.

Chapter 4 summarizes the development of induced nematic phase from the mixture of two purely smectogenic compounds 5-trans-n-pentyl-2-(4-isothiocyanatophenyl)-1,3-dioxane (5DBT) and 4-cyano-4′-*n*-decyloxy-biphenyl (10OCB). A depression of smectic A phase stability occurs in the mixtures with the appearance of an induced nematic phase in a certain concentration range of $0.05 < x_{5DBT} < 0.952$. Within the concentration range $0.252 < x_{5DBT} < 0.696$ smectic A phase completely disappears and only the nematic phase is present. The induced nematic phase is most stable near $x_{5DBT} = 0.696$. The systematic study of the ordinary (n_o) and extraordinary (n_e) refractive indices demonstrate normal temperature variation with a rapid change near the N-I transition. The birefringence value obtained from two different probing methods *viz.* thin prism and optical transmission techniques are in good agreement with a small deviation of about 2-3%. In this chapter specific importance has also been given to the birefringence data near the SmA-N phase transition with the aim of determining the order character of the SmA-N transition. The parameterization of critical behavior of Δn endows with a second order nature of the SmA-N phase transition in all the mixtures except for $x_{5DBT} = 0.100$ for which the same is first order in nature. This induced nematic system also exhibits a uniform crossover of the

SmA-N transition from the 3D-*XY* universality limit to tricritical point. Most importantly, this binary system shows the presence of two tricritical points (TCP) for the SmA-N transition on either side of the phase diagram for x_{5DBT} = 0.123 and 0.894, at which a crossover from second order to first order nature arises. Interestingly, both the TCP concentrations having a common value of the McMillan ratio T_{SN}/T_{NI} = 0.992. However, the 3D-*XY* universal limit for the SmA-N transition is reached almost exactly at x_{5DBT} = 0.696 with a critical exponent value of $\alpha = -0.0068 \pm 0.0004$, for which the McMillan ratio is 0.912.

Chapter 5 is focused on the measurement of free molecular dipole moment of the two pure smectogenic compounds 5DBT and 10OCB of the induced nematic system and static dielectric study of their mixtures. The compound 10OCB with CN terminal possesses slightly higher value of dipole moment than 5DBT with NCS terminal group because the CN terminal group contributes more dipole moment than the NCS terminal group. In the smectic A phase the parallel component of dielectric permittivity shows a prominent decrease for most of the studied mixtures as a result of the dipole-dipole correlation within the mesophase. The effective molecular dipole moment (μ_{eff}) shows an increasing trend with increase in temperature while the angle of inclination (ω) remains almost constant in the low temperature region but increases to some extent near the clearing temperature (T_{NI}). For all the mixtures the isotropic dielectric permittivity (ε_{iso}) shows a strong pretransitional behavior exhibiting a maximum near T_{NI}. This bending of ε_{iso} arises due to different factors such as strength of the transition, correlation of dipole moments and formation of pseudo nematic domains in the isotropic phase. The amount of bending increases for those mixtures where the contribution of 10OCB is greater. This may due to fact that the comparatively higher dipole moment of 10OCB leads to an enhanced pretransitional effect near the transition temperature. On the other hand, the decrease in the isotropic dielectric permittivity very close to T_{NI} is related to the mutual cancelation of the anti parallel ordering of the dipole moment of liquid crystal molecules. The dielectric permittivity data has been parameterized by the fluid like model according to which the N-I phase transition lies on the loci of continuous phase transition curve. For all the mixtures the discontinuity of the N-I transition (ΔT^* =

$T_{NI} - T^*$) demonstrates a systematic concentration dependence. The low value of ΔT^* at N-I transition compared to the same predicted theoretically by the phenomenological Landaue-de Gennes theory entails fluid like critical nature of the N-I phase transition. The critical exponent α is nearly equal to 0.5 which strongly supports the tricritical hypothesis (according to tricritical hypothesis $\alpha = 0.5$) and indicates a first order nature of the N-I phase transition. The results of dielectric measurements have also been verified by high resolution density study for a particular concentration $x_{5DBT} = 0.301$, which results a very much comparable value for both the critical exponent and the width of metastable region at T_{NI}. In addition, the dielectric anisotropy offers a unique way to determine the nature of the SmA-N phase transition. It has been observed that in two mixtures $x_{5DBT} = 0.161$ and 0.203, the SmA-N phase transition is second order in nature while for $x_{5DBT} = 0.100$ SmA-N phase transition is first order through a tricritical point (TCP) located near $x_{5DBT} = 0.120$. This exemplifies an excellent consistency with the consequences extracted from the high resolution birefringence measurements.

Chapter 6 presents high resolution density studies for a polar-non polar binary system comprising of 4-heptyl-4′-*n*-cyanobiphenyl (7CB) and 4–n–pentyl–4′–n′–hexyloxybenzoate (ME6O.5) showing induced smectic A phase. The density data is quite successful in characterizing the pretransitional anomaly near the N-I as well as SmA-I phase transition. The spinodal temperatures T* and T** along a hypothetical continuous phase transition have been determined from a fitting procedure by using the molar volume data. The discontinuity (ΔT^*) at the clearing temperature is found to be considerably higher for SmA-I transition than the same at N-I transition. The extracted values of both $T_{NI} - T^*$ and $T^{**} - T_{NI}$ (or $T_{SI} - T^*$ and $T^{**} - T_{SI}$) supports the tricritical nature of N-I (or SmA-I) transition. Besides, the width of the metastable region *i.e.* $T^{**} - T^*$ for the SmA-I transition is greater than that obtained for the N-I transition, which is in evitable from the comparison of density jumps for both the transitions. A further significant finding is that both the N-I and SmA-I transitions is accompanied by a decrease in the ΔT^* as well as ΔT^{**} with increasing concentration of the polar compound 7CB. The ratio of the two discontinuities ($\Delta T^*/\Delta T^{**}$) is appeared to be non-universal in nature disagreeing appreciably

from the theoretical Landau-de Gennes value. 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. Moreover, the SmA-N transition has also been assessed from the density data and the related outcomes are compared with the same obtained from high resolution birefringence measurements. Both of these independent measurements offer a very good agreement as far as the order of the SmA-N transition is concerned. Significantly, this binary system (7CB+ME6O.5) imparts two tricritical points (TCP) located at x_{7CB} = 0.232 and 0.627 on either side of the phase diagram.

Chapter 7 embraces a detailed study on the orientational order parameter (<P_2>) from the refractive index measurements for a polar-polar binary system exhibiting induced nematic phase in a certain concentration range involving two smectogenic compounds 5-trans-n-butyl-2-(4-isothiocyanatophenyl)-1,3-dioxane (4DBT) and 4-cyano-4′-n-undecyloxy-biphenyl (11OCB). A direct extrapolation technique offers an easy way to determine the orientational order parameter from the birefringence data excluding the prerequisite of molecular polarizability and density values. The N-I transition is accompanied by a sharp increase of the order parameter, demonstrating a first order character of the N-I phase transition. On decreasing the temperature, a gradual increase in <P_2> value has been observed owing to the enhanced molecular ordering in the nematic as well as smectic A phase. In contrast, the smectic A-nematic (SmA-N) phase transition is accompanied by continuous change in the order parameter except for x_{4DBT} = 0.884. A sharp change in the order parameter near the SmA-N transition temperature (T_{SN}) indicates a first order nature of the SmA-N phase transition for x_{4DBT} = 0.884. Although in rest of the mixtures SmA-N transition is second order in nature. A comparison of the <P_2> values with the same obtained from Maier-Saupe and McMillan mean field theory demonstrates the fact that at very close to T_{NI} the <P_2> values drop more rapidly than the theoretical mean field value and the quality of agreement between the theoretical and experimental <P_2> value is poor. However, far from the transition, the experimental <P_2> values can be well described by the theoretical mean field curves for most of the mixtures and the consistency between the two sets of values is quite good. Moreover, the Haller

type fitting expression results a very low value of the order parameter critical exponent β but using the four parameter fitting expressions to the optical as well as dielectric anisotropy (Δε) data this difficulty has been surpassed, resulting a consistent β values very close to 0.25, the tricritical value. The consistency of the β value with that predicted by the tricritical hypothesis (TCH) is particularly very imperative because it describes the global behavior of the nematic order parameter. Thus, the four parameter power law expression works much better than the Haller type expression as far as the order parameter critical exponent β is concerned. Again β values obtained from the dielectric anisotropy (Δε) show an excellent agreement with those obtained from the optical anisotropy (Δn).

Chapter 8 is concentrated on the detailed study of splay elastic constant (K_{11}) and rotational viscosity (γ_1) for the binary system 4DBT+11OCB. On the basis of electric field induced Freedericksz transition the threshold voltage V_{th} has been calculated which increases substantially with decreasing temperature. The splay elastic constant exhibits normal temperature behavior in the nematic phase for most of the concentrations except for x_{4DBT} = 0.787 and 0.884 which encompasses a stiffening of the same as the SmA phase is approached. The relaxation time (τ_0) shows a noticeable decrease with increasing the concentration of 4DBT in the range 0.393 to 0.707. This may happens because of a lesser amount of inter-molecular packing of the two mesogenic compounds with dissimilar core unit. Also the rotational viscosity (γ_1) demonstrates similar trend as exhibited by τ_0. Existence of 4DBT with heterocyclic oxygen atom in the core structure interrupts the molecular packing through the structural incompatibility and causes a reduction in the rotational hindrance of the composite system. Again γ_1 is not linearly dependent on the concentration as the microscopic friction of the binary mixtures depends on the concentration of the LC compounds in a complex way. Interestingly, in the neighborhood of the SmA-N phase transition the variation of γ_1 for x_{4DBT} = 0.208, 0.291, 0.707, 0.787 and 0.884 primarily snatches the attention due to a pretransitional behavior arising from the fluctuations of smectic like short range ordering within the nematic phase. The critical exponent ν associated with γ_1 near the SmA-N transition have been found to be quite comparable to 0.33, indicating a deviation from the corresponding mean field

exponent ($\nu = 0.5$). Moreover, for the present binary system the activation energy for rotation in the nematic phase is relatively lower in the region of maximum nematic phase stability.

There are numerous interesting and promising areas which can be explored further. Study of the other phase transitions like smectic A to smectic C, nematic to smectic C, nematic to smectic C* *etc.* would be very much exciting to understand the transitional order and the universality class of the associated critical exponents. In addition, a more challenging work would be to realize the effect of the range of different mesophases on the nature of the above said phase transitions. Continuous research efforts are required to further comprehend the critical behavior of those systems. Moreover, the experimental work focused on the induction of different liquid crystalline phases other than the nematic and smectic A phase also deserves some attention. This type of study may produce novel binary phase diagrams exhibiting various mesophases and physical properties. Nowadays an emerging area in the field of soft condensed matter physics is the nano-dispersed liquid crystalline systems. The critical behavior of the nano doped liquid crystal systems is also an unexplored area from the phase transition point of view. Further work in this direction may be carried out to deal with the above mentioned problems.