

Chapter VIII

SUMMARY AND CONCLUSIONS

The studies on Liquid Crystals over the years have significantly increased because of its wide applications. For successful application of liquid crystals its physical properties must fulfill certain criteria. Single component liquid crystal usually does not fulfill such conditions, as a result mixtures are used in commercial display devices. Sometime new phases are induced in mixtures which were not present in the pure components making them interesting systems to investigate. In addition to the calamitic thermotropic systems, ferroelectric liquid crystals are nowadays used for new generation of fast versatile liquid crystal devices. In this context studies on different physical properties of the pure and binary liquid crystal systems and understanding them in relation to their structures are important. Keeping this in view several physical properties of eighteen mixtures of three binary systems have been studied in the thesis by employing optical microscopy, DSC, X-ray diffraction techniques as well as optical birefringence and dielectric constants measurements. Ratio of splay to bend elastic constants of some mixtures has also been determined. Moreover, frequency dependence dielectric spectroscopy studies have been made on a fluorinated analogue of the prototype antiferroelectric liquid crystal MHPOBC. Crystal and molecular structure of a four-ring compound has been determined for deeper understanding of its phase behaviour. A chapter wise summary and important conclusions are given below.

In Chapter I, an introduction to the field of liquid crystals has been given particularly the thermotropic liquid crystal systems. Different types of liquid crystals viz., nematic, smectic A, smectic B and other smectic like soft crystal phases as well as ferroelectric liquid crystals have been described briefly. Emphasis has been given on discussions on the nematic, induced smectic A, ferroelectric liquid crystals which have been studied in the present work. A brief review of applications of liquid crystals in various fields have also been described. List of the pure compounds and the binary systems investigated in the thesis are also given.

In Chapter II, Maier-Saupe mean field theory of nematic phase and McMillan's theory of smectic A – nematic phase transition have been discussed since some of the experimental results have been compared with the observations of these theories. Theory of X-ray diffraction from liquid crystals and methods of

analysis of X-ray photographs have been given. Relevant theory to calculate various molecular parameters have been described in detail. Maier-Meier and Bordewijk theories of dielectric properties of liquid crystals and theoretical basis of the calculation of effective molecular dipole moment and dipole-dipole correlation factors in the nematic phase have also been discussed. Theoretical background of the elastic deformation of liquid crystals have been given. Theory of crystal structure analysis by direct methods from CAD4 diffractometer data have also been outlined. Details of all the experimental set ups and procedures adopted have been described.

In Chapter III, phase diagrams of three binary mixture systems have been presented. The systems consist of a strongly polar compound 5OCB as guest in a weakly polar host nOAB with $n=5-7$. All these compounds are nematogenic, only 7OAB exhibits also SmC phase. Optical microscopy, DSC and X-ray diffraction techniques were applied to establish the phase diagrams. Seven mixtures (A_1 to A_7) of concentrations $x_{5OCB}=0.15, 0.25, 0.35, 0.50, 0.65, 0.75$ and 0.875 for the system (5OCB+5OAB), five mixtures (B_1 to B_5) of (5OCB+6OAB) at concentrations $x_{5OCB}=0.15, 0.25, 0.50, 0.75, 0.85$ and six (C_1 to C_6) of (5OCB+7OAB) system with concentrations $x_{5OCB}=0.12, 0.15, 0.25, 0.50, 0.75$ and 0.85 were prepared. It is observed that whenever a small amount of 5OCB is introduced in the host 6OAB or 7OAB induction of SmA phase takes place. In case of 5OAB, mixing of 15% or more 5OCB molecules induces SmA phase. Over a wide concentration range (about $x_{5OCB}=0.25$ to 0.75) the nematic phase of the pure components is completely suppressed. Maximum thermal stability of the induced SmA phase is observed to be 86.4°C in the equimolar mixture B_3 which is 78.1°C in A_3 and 80.1°C in C_3 . No SmC is observed in any of the six C mixtures though the host 7OAB possesses this phase. Change in enthalpy at SmA-I transition, in all the mixtures, is found to be non-additive.

From the X-ray diffraction photographs inter-molecular distance 'D', apparent molecular length 'l' in N phase and layer spacing 'd' in SmA phase are calculated. The D values in all the mixtures increases with temperature. There is not much difference in D values of the three mixtures. The average value is 4.95 \AA .

With increasing concentration of the polar component the D value in all the mixtures decreases to a minimum and then increases, however, the D values are more in the mixtures than in the pure components. The observed ' l ' values in the mixtures A and B do not differ much from those of the pure compounds whereas in C these are larger than those of the pure compounds.

In the mixtures A the ' d ' values vary from 22.2 to 24.8 Å, between 23.0 Å and 25.8 Å in mixture B and between 25.0 Å to 29.0 Å in C. We calculated ' d ' values by additivity rule considering both the pure components exist as monomers in model 1 and considering that the system to be made up of 5OCB dimers and n OAB monomers in model 2. Calculated and the observed ' d ' values suggest that in all the three binary systems at higher concentrations 5OCB molecules exist as dimers whereas at lower concentrations they are mostly in monomeric form as if SmA_d phase is evolving from SmA_1 phase.

In Chapter IV, the results of the optical birefringence and density measurements on the above mixtures are presented. It is observed that in both the mixtures B and C the nature of variation of n_o , n_e and \bar{n} with concentration is different than in the mixtures A. All the parameters - n_o , n_e and \bar{n} - in mixtures A lie in between the values of the pure compounds except in A_1 in which these are more and in A_4 where these are less than the pure compounds. However, in mixtures B and C all these parameters are less than both the pure components in all concentrations (except in C_5 where these are more). Moreover, values of the refractive indices are less in the induced SmA phase than in the nematic phase in all cases. Temperature variation of n_o and n_e is less in induced SmA phase than in N phase. The average refractive index (\bar{n}) remains almost constant with temperature but a discontinuity is observed at $SmA-I$ and $N-I$ transition points.

In the mixtures A, B and C the values of Δn are found to decrease systematically with concentrations. Moreover, it is also observed that the range of variation of Δn decreases as one moves from the mixture A to C. Temperature variation of Δn is also similar in all the mixtures. It decreases slowly in low T

region, thereafter the decrement rate increases becoming very fast near the T_{NI} or T_{SI} transition point.

In mixtures A the densities are found to be less than those of the pure compounds except in A_7 , in mixtures C densities lie in between those of the pure components and in B the density values do not vary systematically relative to the pure compounds. Within the mesomorphic range of the pure components densities of the three equimolar mixtures are less than those of 5OCB and 5OAB and lie in between those of 6OAB and 7OAB. Outside this range, however, the density increases from mixture A onwards, though in the pure components the density decreases with chain length. This has been tried to explain by considering the packing of the 5OCB monomers and dimers in nOAB hosts.

The polarizability anisotropy of the three mixtures varies systematically with increasing concentration of 5OCB. The anisotropy value of the mixtures lies between the pure component values. The orientational order parameters ($\langle P_2 \rangle$), calculated from the polarizabilities, are found to be more in smectic phase than in N phase as expected and temperature variation of OOPs is less in smectic phase than in N phase. Large $\langle P_2 \rangle$ values are observed in SmA phase in the middle of the phase diagram because thermal stability of the injected smectic phase is more in this region. The observed orientational order parameters are compared with values obtained from McMillan's theory in SmA phase and MS theory in N phase. In Mixtures A and B reasonable agreement is observed between the experimental and the McMillan order parameters except in N phase while for mixtures C the fitting is poor. The transition temperatures obtained from McMillan's theory differ from the observed values by a maximum of $\sim 5^\circ\text{C}$. In mixtures A and B the OOP remains almost constant over a considerable range of concentrations around the equimolar value but in C after an initial increase it decreases continuously. Elastic constants determined only in nematic phases are found to be more than in pure compounds and diverges as T_{N-SmA} is approached.

In Chapter V the static dielectric properties of the above 18 binary mixtures have been studied in detail. The polar component of the mixture i.e. 5OCB has a large positive dielectric anisotropy while nOAB members have small but

negative anisotropy. However, all the mixtures exhibit positive anisotropy. When only 15% of the host nOAB molecules are replaced by the guest 5OCB molecules dielectric parameters (ϵ_{\parallel} , ϵ_{\perp} and $\bar{\epsilon}$) increase considerably from those of pure nOAB and a cross over from negative to positive dielectric anisotropy takes place. At the onset of the SmA phase the parameters decrease from their values in N phase. This is a result of development of additional antiferroelectric ordering of the molecular dipoles in the stratified smectic structure. However this lowering of the ϵ values is surpassed by the increased polarizability values when concentration of 5OCB molecules becomes 50% or more, as a result the dielectric parameters start increasing. With increasing temperature, this additional antiferroelectric type ordering in SmA phase gradually decreases and so ϵ values increase with T . In all the mixtures the anisotropy parameter $\Delta\epsilon$ decreases with concentration, becomes minimum at $x_{5OCB} = 0.5$ and then increases quite fast. Thus the observed value of $\Delta\epsilon$ do not follow the simple additivity rule. Moreover, the nature of concentration and temperature variation of $\Delta\epsilon$ is different from that of Δn .

In all mixtures the values of ϵ_{iso} are found to be higher than the $\bar{\epsilon}$ values within the mesophases with a jump at T_{NI} or T_{SI} . This again suggests the presence of antiferroelectric type ordering in both smectic and nematic phases which decreases in the isotropic phase. This conclusion is further supported by the fact that the effective values of the dipole moments, calculated from the Maier-Maier theory, in the mesophases of the mixtures are found to be less than the values observed in the pure compounds. The Kirkwood correlation factors g_{\parallel} and g_{\perp} have also been calculated and following observations are made on the nature and extent of the molecular associations. In mixtures having only nematic phase the components of the effective dipole moment parallel to the molecular axes are arranged in slightly antiparallel manner at low temperature, as the temperature is increased these correlation gradually disappear. On the other hand, at low temperature the perpendicular components of the effective dipole moment are arranged in almost perfect anti-parallel fashion. This correlation gradually decreases with temperature but not completely destroyed even at high temperature. In mixtures with smectic

phase similar type of correlation exists at low temperatures, only the extent of correlation is changed.

In Chapter VI, optical microscopy, DSC, spontaneous polarization and frequency domain dielectric spectroscopy of a partially fluorinated ferroelectric liquid crystalline compound MHPO(13F)BC which is a prototype of anti-ferroelectric compound MHPOBC, are presented. Broken fan texture was observed in SmA* phase. Helix unwinding lines were observed in SmC* phase. A slightly different texture, but with distinctly different birefringence colour, was observed in between the above two phases. However, DSC measurements could not detect any such phase change. But an anomalous thermal behaviour in P_S and in the dielectric strength ($\Delta\epsilon$) was observed in between the SmA* and SmC* phases. This may be due to the presence of SmC $_{\alpha}$ * phase. No signature of presence of SmC $_A$ * is found in this compound. Combining the optical microscopy, DSC and dielectric results the following phase sequence is proposed for **MHPO(13F)BC** during cooling. Cr1 91.5 SmC* 141.4 SmC $_{\alpha}$ * 145.5 SmA* 180.8 I.

From the frequency dependence dielectric spectra clear evidence of Goldstone mode is observed in SmC* and SmC $_{\alpha}$ * phases. Fitting the spectra to Cole-Cole function the critical frequencies are found at 3.1 and 7.2 kHz respectively. The GM modes could be suppressed by applying a bias field and clear evidence of the Soft mode was seen in the spectra. Critical frequencies are found to be 22.1 and 9.9 kHz in SmC* and SmC $_{\alpha}$ * phases respectively by fitting the spectra to the Cole-Cole function. This is 55.6 kHz in SmA* phase.

In Chapter VII, the crystal structure of a compound 4-cyanobiphenyl-4'-hexylbiphenyl carboxylate (6CBB), which exhibit both monolayer smectic A and nematic phases, has been determined by direct methods using single crystal X-ray diffraction data. Full-matrix least-squares refinement on the structure factors (F), with anisotropic temperature factors for the non-hydrogen atoms and isotropic for the hydrogen atoms, converged to R=0.076, Rw=0.074. Final difference Fourier map revealed a residual electron density between -0.25 and 0.28 eÅ $^{-3}$.

The structure is triclinic with the space group $P\bar{1}$ and $Z=2$. The unit cell parameters are $a=9.3511(7)$ Å, $b=11.2456(7)$ Å, $c=13.1417(6)$ Å, $\alpha=85.872(4)^\circ$, $\beta=76.258(5)^\circ$ and $\gamma=70.697(5)^\circ$. The calculated length of the 6CBB molecule in the crystalline state is 27.83 Å whereas the model length in the most extended form is 30.6 Å. Thus the molecule is found to be slightly bow-shaped though the alkyl chain is in all-*trans* conformation. The observed bond distances and angles agree well with the values reported for similar mesogenic materials. Individually all the four phenyl rings are planar but they are not coplanar. The direction cosines of the molecular long axis, defined as the best fitted line through all the atoms, are found to be 0.31, -0.58 and 0.75. Thus the long axis of the 6CBB molecules is inclined to the orthogonal X, Y and Z axes at angles 72, 125 and 41° respectively. The pair of molecules related by the centre of inversion are arranged in parallel manner. These pairs of parallel molecules are packed in inter-penetrating layers. On heating opposite shift of the pairs parallel to each other by half the b-axis may give rise to SmA layer structure. Thus packing of the 6CBB molecules in the crystalline state is precursor to the SmA phase structure, which on further heating may adopt the nematic structure. Crystal to SmA transition is, therefore, of 'displacive' type rather than of 'reconstitutive' nature where in addition to the translational motion rotation about an axis other than the molecular long axis is also necessary for the transition.

Calculation of intermolecular distance between molecules related by centre of symmetry reveals existence of numerous van der Waals interactions. Three different types of molecular associations in head-to-tail configuration are observed (i) Molecules of the pair overlap almost completely so that the cyano groups lie at the opposite ends (ii) Molecules of the pair overlap almost completely but the three end atoms of the hexyl chain lie at the opposite ends (iii) Only the core regions of the two molecules of the pair overlap but not the hexyl chains. Pair of the second type may easily give rise to SmA₁ structure. Though the length of the pair of the first type is nearer to the observed smectic layer spacing than the length of the second type, it is easier to obtain smectic layer structure by translations of the second type pair rather than the first type. It is inferred that the subtle difference in the

interaction between neighbouring molecules as a result of steric effect might be the origin of developing monolayer SmA_1 phase in four ring cyano compound 6CBB and partially bilayer SmA_d phase in two ring cyanocompounds.