Experimental Studies on Phase Diagrams of Liquid Crystals

by

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Thesis submitted to the Jawaharlal Nehru University for the degree of Doctor of Philosophy

2004

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DECLARATION

I hereby declare that this thesis is composed independently by me at the Raman Research Institute, Bangalore, under the supervision of Prof. N. V. Madhusudana. The subject matter presented in this thesis has not previously formed the basis of the award of any degree, diploma, associateship, fellowship or any other similar title in any other University.

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CERTIFICATE

This is to certify that the thesis entitled **Experimental Studies on Phase Diagrams of Liquid Crystals** submitted by V. Manjuladevi for the award of the degree of DOCTOR OF PHILOSOPHY of Jawarharlal Nehru University is her original work. This has not been published or submitted to any other University for any other degree or diploma.

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PREFACE

In this thesis we present our experimental studies on phase diagrams of liquid crystals. We have modified a high pressure optical setup which was available in the laboratory, to measure the optical path difference of aligned liquid crystals. Using this setup we have studied various types of liquid crystal phase transitions such as nematic-nematic (N-N) transition, uniaxial smectic A to biaxial smectic A transition, TGB_A to $UTGB_C^*$ transition etc. We have also estimated the temperature variations of birefringence of some liquid crystals along various isobars. Mesogens with highly polar end groups exhibit a variety of interesting phase transitions. An interesting example is N-N transition which is a weak first order transition with no change in the macroscopic symmetry between the two nematics, but with a change in the short range ordering of the molecules. We report the evidence for an N-N transition in the bulk of a polar compound at *elevated* pressures. We report a *new* type of nematic-nematic (N-N) transition in binary mixtures of polar compounds at *atmospheric pressure*. We show that the nematic-nematic transition temperature decreases with increasing thickness in *planar* aligned cells. The birefringence measured in *planar aligned thin* cells is enhanced compared to that measured in thick cells. In homeotropically aligned cells the N-N transition temperature is found to be *independent* of cell thickness. We also present the concentration temperature phase diagram of the above binary mixture of polar compounds. We have developed a new technique of subjecting liquid crystals to negative pressures by embedding them in a glassy matrix of sucrose. We report the *first* measurements of birefringence on isochoric cooling of liquid crystals, which will be under tension.

A general introduction to liquid crystals of various classes and their physical properties relevant to our study is given in **Chapter 1**.

Phase transitions in liquid crystals are usually studied by varying temperature at atmospheric pressure. However, as the liquid crystalline materials are soft, even moderately high pressures often have a strong influence on the transition temperatures. In **Chapter 2** the modification of a high pressure optical setup which was available in the laboratory is described. In the earlier high pressure (HP) studies conducted in our laboratory [1], the phase transitions were studied using an optical

transmission technique, but no optical path difference measurements were made. We have modified the optical setup so as to measure the *optical path-difference* and hence the birefringence as functions of both temperature and pressure. Such a measurement allows to investigate the effect of pressure on very weak phase transitions with ~1% jump in the order parameter as in the nematic-nematic transition. Any minor change in the transmitted intensity data due to source fluctuations can be misleading. Hence to take into account the source fluctuations we have exploited a facility called dual reference mode provided by the lock-in amplifier (LIA: EG&G lock-in amplifier model 7260), using which two optical signals at different frequencies can be simultaneously measured. A laser beam is split into two beams and made to pass through two different windows of the same chopper (EG&G model 198). One of the beams is allowed to pass through the sample kept between crossed polarisers and the other beam is treated as the reference beam and then both of them are combined using a beam combiner. A single photodiode is used to detect both the signals using the LIA (Figure 1). The ratio of transmitted intensity signal to reference signal is used as the data for further analysis. The whole setup is automated such that along with temperature control, intensity data at regular temperature steps are also collected using a PC.

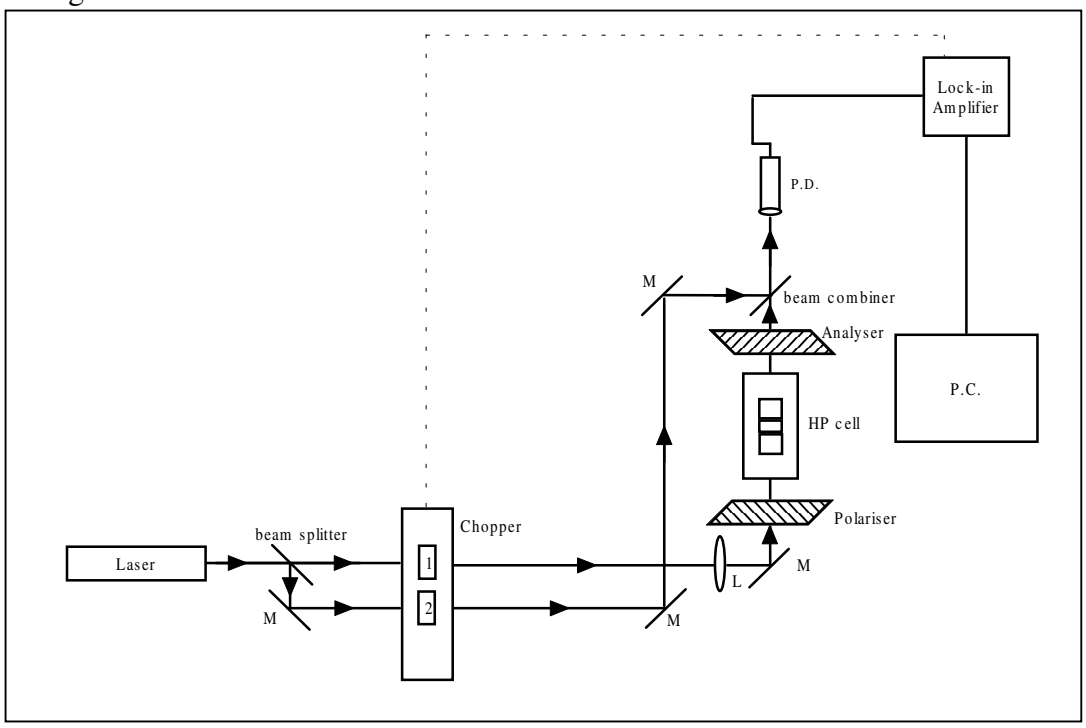

Figure 1: Schematic diagram of the modified high pressure optical setup: M-mirror, L-lens, P.D. – photodiode, P.C. – personal computer.

In the earlier high pressure optical studies [1] the liquid crystal sample was sandwiched between optically polished sapphire windows which are birefringent. For optical path difference measurements we use the optically isotropic *fused quartz* windows treated for planar alignment and enclosed in a fluran tube. A mylar spacer is used to fix the thickness of the sample. The temperature is controlled to an accuracy of 25 mK, using a suitable software program which also records the intensity signals at various temperatures. The accuracy of pressure measurement made using a Bourdon type HEISE gauge is about 5 bars.

The temperature calibration of the high pressure (HP) optical setup is made by studying the phase transitions of standard samples in the HP optical cell. High pressure studies on 8OCB (Octyloxy cyanobiphenyl) were conducted to make the calibration of HP cell. The pressure-temperature (P-T) phase diagram of 8OCB constructed by us is in good agreement with that reported by Cladis et al [2].

The following new results are reported in this chapter:

- Estimation of birefringence $\Delta\mu$ as a function of temperature along various isobars of a few compounds (Figure 2).
- Estimation of order parameter S as a function of temperature along various isobars using the birefringence data fitted to Haller's extrapolation formula [3].

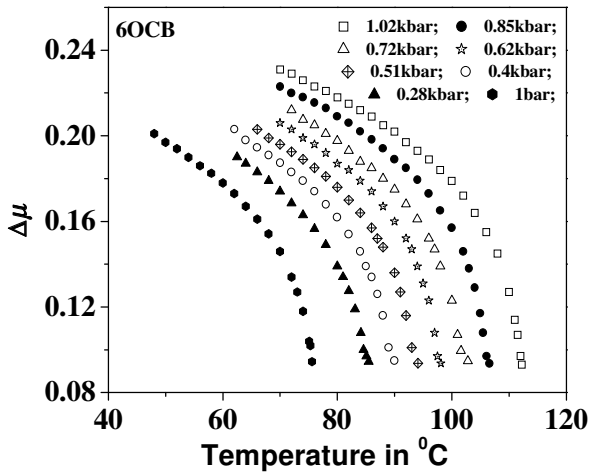

Figure 2: Temperature variations of the birefringence $\Delta\mu$ of 6OCB at various pressures.

In **chapter 3** we discuss the effect of pressure on N-N transition in a pure nematogen. Mesogens with highly polar end groups exhibit a variety of phase transitions [3,4]. An interesting example is the Nematic-Nematic (N-N) transition which is a *weak first order transition* as the macroscopic symmetry of the two nematics is the same, but with a change in the short range ordering of the molecules. Using specific heat measurements a N-N transition observed as a continuation of SmA_1-SmA_d transition line in a binary mixture of polar compounds was reported by Nounesis et al [5]. A molecular theory of this transition [6] has predicted that at low temperatures or high densities a change in the intermolecular configuration from antiparallel (N_d) to parallel association of molecules (N_1) can take place. This leads to a *polar short range* order in the medium. Indeed such a polar short range order has been earlier reported in case of a compound with a CN end group, viz., p-cyanophenyl p-n-heptyl benzoate (CP7B) [7]. On application of electric field of ~ 600 esu strength to a 10 μm cell of CP7B, Basappa et al [7] had observed the N-N transition around 33 ^{0}C. Subsequently Sobha et al [8] had observed that the N-N transition takes place in *planar aligned thin cells* (1.5–3 μm) of CP7B at atmospheric pressure. The N-N transition temperature increases with decreasing thickness of the sample [8]. In both the above cases the N-N transition occurs for a high value of order parameter. However, this transition is not observed in the bulk of CP7B in absence of any field as the orientational order parameter would not reach the required high values. On compression the density of the medium and the orientational order increase. We conducted high pressure studies on CP7B. Indeed we have observed that the N-N transition in bulk (~12 μm) of CP7B takes place at temperatures well above the ambient at *elevated* pressures. The P-T phase diagram of CP7B is shown in Figure 3 in which Nematic - Isotropic (NI) transition temperature as well as N-N transition temperature as functions of pressure are presented. The N-N transition temperature increases linearly with increasing pressure. The measured values of $(dP/dT)_{NI}$ and $(dP/dT)_{NN}$ are 30 bar/^{0}C and 58.9 bar/^{0}C respectively. We also present the temperature variation of birefringence of CP7B at various pressures.

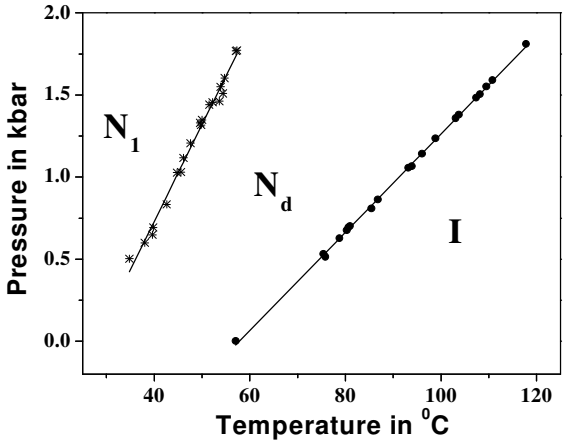

Figure 3: The pressure-temperature phase diagram of CP7B. The nematic phase occurring at temperatures above T_{NN} is indicated by N_d and that at lower temperatures by N_1.

It is convenient to have a system which exhibits the N-N transition at atmospheric pressure at temperatures well above the ambient so that many other experiments can be conducted. We have found that certain binary mixtures of polar compounds exhibit such behaviour. We have prepared some binary mixtures of CP7B with another polar compound 4-[5-(4-butyl-phenyl)-pyrimidin-2-yl]-benzonitrile (4PCPP). The mixture with 70.5 mol% of CP7B with 4PCPP exhibits the NN transition. The N-N transition temperature increases with decreasing thickness of the sample in agreement with the earlier studies on a pure compound [8]. As the compound CP7B was in short supply, we did not carry out further studies on this binary mixture.

CP6B, the lower homologue of CP7B also has a large longitudinal dipole moment, but a very narrow nematic range. In **chapter 4**, we present detailed studies on binary mixtures of CP6B with 4PCPP. Though we do observe a nematic-nematic transition in these mixtures, we have experimental evidence to show that it does not correspond to the N_1N_d transition. It is indeed a *new type* of nematic- nematic transition. We have carried out X-ray diffraction studies on one of the binary mixtures and found that the measured layer spacing *d* of short range ordered groups corresponds to a *partial bilayer structure* and remains a constant throughout the nematic range. In view of this result we call this *new* type of N-N transition as N_lN_h transition associated with a change in the concentrations of different types of short

range ordered groups of molecules, all with antiparallel association. The symbol N_l represents the nematic phase at low temperature and N_h, the nematic phase at high temperatures. We have carried out light scattering experiments on *homeotropically* aligned samples observed between crossed polarisers. The intensity of light scattered by the sample is monitored in a narrow range of angles near the forward direction. The N_lN_h transition shows up as a peak in the scattered intensity (Figure 4).

In *homeotropically* aligned cells:

- The transition N_lN_h temperature is found to be independent of cell thickness.
- A substantial slowing down of director fluctuations is observed near the N_lN_h transition point indicating that it is close to a critical point.
- The measured dielectric constant $\varepsilon_{||}$ using the homeotropically aligned cells however does not show any signature of N_lN_h transition.
- Dielectric relaxation of $\varepsilon_{||}$ occurs at very low frequencies (Figure 5).
- The measurements of relaxation frequency indicate that the strength of nematic potential felt by the molecule with longer aromatic core is lower at higher temperatures than that felt at lower temperatures indicating a change in short range order in the medium.

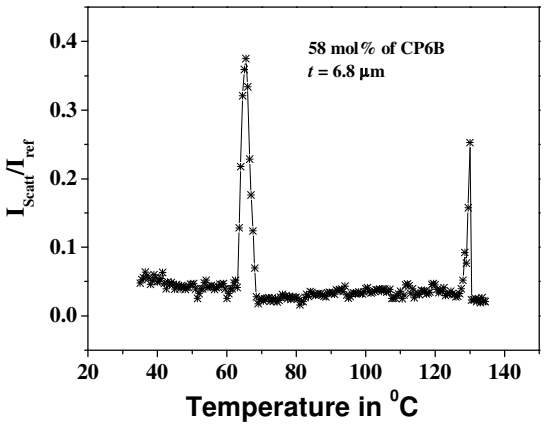

Figure 4: The variation of the ratio of scattered intensity to reference intensity as a function of temperature for a mixture with 58 mol% of CP6B in a cell of thickness t = 6.8 µm.

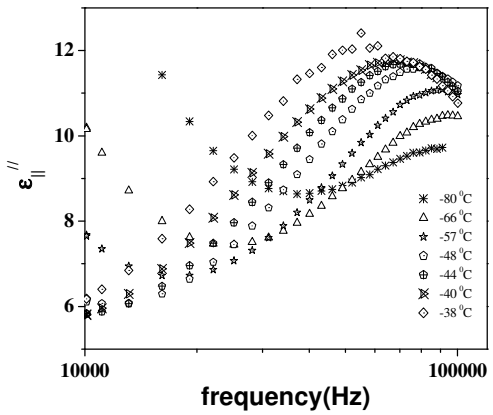

Figure 5: The variation of the dielectric loss (imaginary part of the dielectric constant) $\varepsilon''_{||}$ as a function of applied frequency (plotted in a logarithmic scale) for a mixture with 58 mol% of CP6B in a cell of thickness t = 6.8 μm. The effect of ionic impurities in the sample is dominant at low frequencies.

We have also carried out optical path difference measurements on a binary mixture with 65 mol% of CP6B contained in *planar* aligned cells of various thicknesses.

In *planar* aligned cells:

- The $N_l N_h$ temperature *increases* with decreasing thickness t of the cell (Figure 6).
- The birefringence $\Delta\mu$ measured in thin cells is enhanced compared to those measured in thick cells (Figure 7).
- The jump in the value of $\Delta\mu$ at $N_l N_h$ transition rapidly *decreases* with increasing thickness of the cell (Figure 8). The strength of the first order transition *decreases* with increase of the cell thickness t, which acts as an external control parameter and at some critical thickness t_c, the transition ends in a *critical point*. Beyond t_c, the medium continuously evolves from one type of nematic to the other.

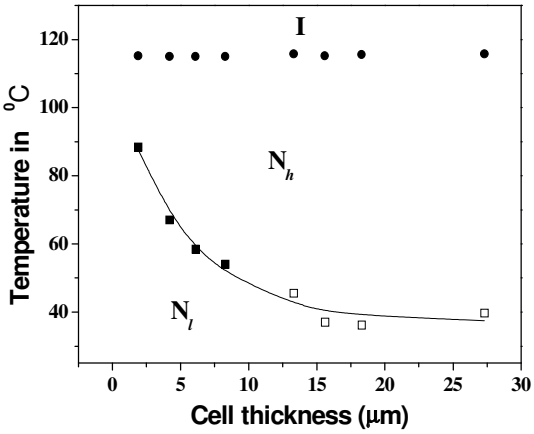

Figure 6: The variations of N_hI and N_lN_h transition temperatures as functions of sample thickness for the mixture with 65 mol% of CP6B. The symbol ■ corresponds to experimental data on cells with $t \leq 8.4$ μm (exhibiting a jump in the transmitted intensity) and □ corresponds to $t > 13$ μm (exhibiting a dip in the transmitted intensity). The solid line corresponds to a least squares fit to an exponential function.

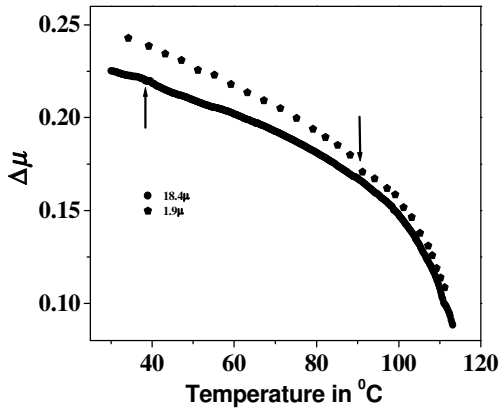

Figure 7: Temperature variations of birefringence $\Delta\mu$ of the binary mixture with 65 mol% of CP6B for cells of thicknesses 18.4 μm and 1.9 μm. The N_lN_h transition is indicated by arrows.

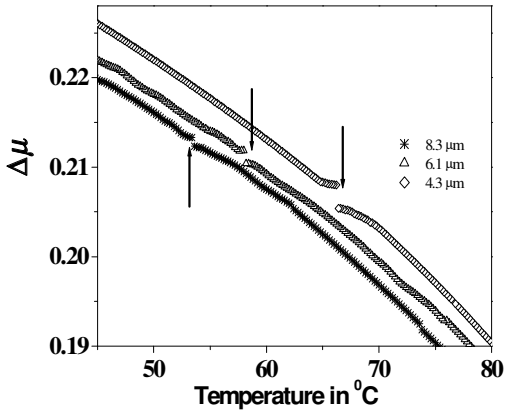

Figure 8: Temperature variations of the 'birefringence' $\Delta\mu$ of binary mixture with 65 mol% of CP6B on an expanded scale around N_lN_h transition for cells of thicknesses 4.3 μm, 6.1 μm and 8.3 μm. The N_lN_h transition is indicated by arrows.

The phase diagram of the binary mixtures in both homeotropic and homogeneously aligned cells of thickness with $t \simeq 19$ μm in the latter case, is presented in Figure 9. The N_lN_h transition temperatures in planar aligned thick samples with $t \simeq 19$ μm for all the compositions on which measurements have been carried out are lower than those observed for homeotropically aligned samples. The N_lN_h transition temperature increases linearly with decreasing concentration of CP6B. But for homeotropically aligned cells the variation shows a minimum at a composition ~ 62 mol% of CP6B.

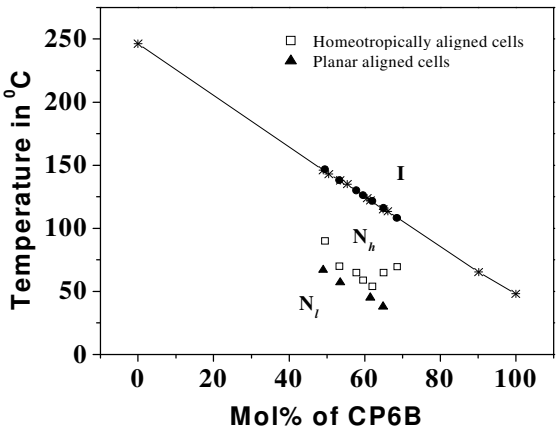

Figure 9: The concentration-temperature phase diagram of binary mixture of CP6B and 4PCPP. The transition temperature data from both homeotropically aligned as well as planar aligned cells are given for comparison.

In **chapter 5** we discuss the effect of positive pressures (compression) on various liquid crystal phase transitions, which also include those for which the data are needed for analysis of negative pressure experiments to be reported in the next chapter. During these investigations we found that an *excess pressure* is generated when a sample in the fluid state is mounted in the high pressure cell as the volume is fixed (due to the method of sample mounting in the high pressure cell).

The following studies are reported:

(i) Pratibha et al [9] have reported that a binary mixture of 1,3-phenylene-bis[4-(3-methylbenzoyloxy)]-4' -n-dodecylbiphenyl-4' -carboxylate (BC12), a banana shaped compound and 8OCB , a compound with rod-like molecules exhibits a variety of interesting phase transitions. In a narrow range of concentrations of 10 to 24 mol% of BC12 the binary mixtures exhibit the biaxial Smectic A (SmA_{db}) phase. Through X-ray studies the authors have confirmed that the rods form a partial bilayer structure of 8OCB molecules in the SmA_{db} phase in this binary mixture. We have carried out HP measurements on a binary mixture of 14 mol% of BC12 with 8OCB. The P-T phase diagram of this system is shown in Figure 10. The value of dP/dT_{NI}=30 bar/^{0}C. The transition temperatures of SmA_d-N, SmA_{db}-SmA_d transitions also vary linearly with pressure.

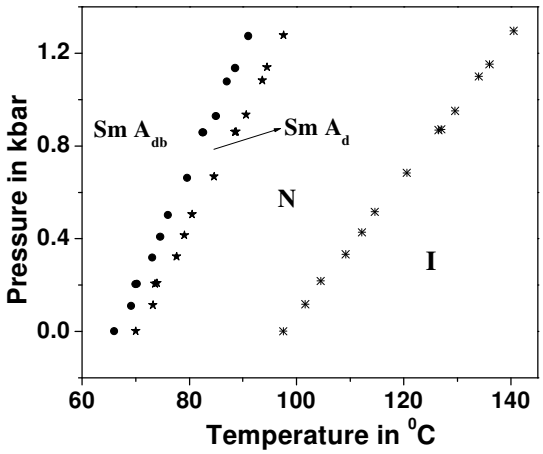

Figure 10: The Pressure-temperature phase diagram of a binary mixture of 14 mol% of BC12 with 8OCB.

(ii) The discovery of a new phase called the undulated twist grain boundary smectic-C* (UTGB$_C$*) was reported on binary mixtures of a *chiral* compound 4-(2′-methyl butyl) phenyl 4′-n-octylbiphenyl- 4-carboxylate (CE8) and a *nonchiral* compound 2-cyano 4-heptylphenyl 4′-pentyl 4-biphenyl carboxylate (7(CN)5) from our laboratory by Pramod et al [10]. We have presented the P-T phase diagram of a binary mixture exhibiting TGB$_A$ and UTB$_C$* phases, in which the TGB phases get bounded at elevated pressures (Figure 11).

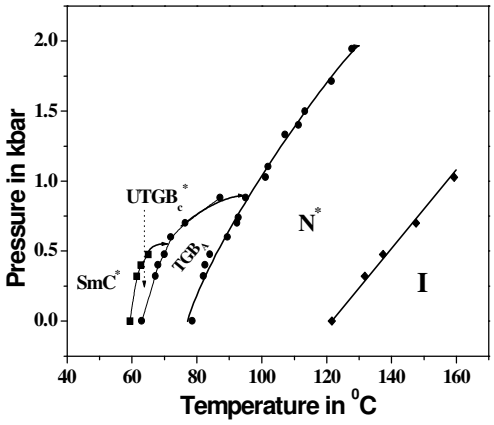

Figure 11: The pressure-temperature phase diagram of a binary mixture of 36 wt% of 7(CN)5 with CE8.

Condensed matter can also sustain *negative pressures* because of attractive interactions between molecules. Under negative pressures the intermolecular distance *r* increases, and the medium which is under tension is in a *metastable* state [11]. To achieve large negative pressures small drops have to be cooled under constant volume (i.e., isochoric) conditions. As the temperature is lowered, such a medium will have a density which is *lower* than in equilibrium. The medium experiences a tensile stress, which increases in magnitude as the temperature is lowered. The medium goes over to the stable state by cavitation, i.e., by developing a vapour bubble [11]. We report phase transitions in liquid crystals under tension in **chapter 6**. In 1990 Zheng et al [12] developed a technique for creating very large negative pressures (~1kbar) by isochoric cooling of small water drops embedded in quartz crystals. In liquid crystals, there is the possibility of studying both the phase transition as well as the *orientational order parameter* under tension. Organic compounds cannot withstand high temperatures used to encapsulate water. We have developed a new technique of

embedding small liquid crystal droplets in a glassy matrix, in which they can be subjected to negative pressures on isochoric cooling. We have found sucrose, a carbohydrate with glass transition temperature T_g ~ 78 ^{0}C, which does not dissolve in most of liquid crystals with phenyl rings to be suitable for this purpose. We have prepared the sandwiched sample using Indium Tin Oxide (ITO) coated glass plates which are pretreated for planar alignment so that the mesophase drops will be aligned homogeneously allowing us to measure the optical path difference. We have taken care so that the sample is present only in the center leaving an air gap all around. The thickness is measured in the surrounding air gap, which allows us to calculate the birefringence $\Delta\mu$ of the medium as a function of temperature in both isochoric as well as isobaric conditions. For the *first* time we have measured the orientational order parameter of mesophases under isochoric conditions. We have also estimated the negative pressure to which the mesophase is subjected. We have also carried out an experiment to measure the splay elastic constant of the medium under tension.

The systems used for study are (i) p-cyanophenyl trans-4-butyl cyclohexane carboxylate (CBCC) with phase transition sequence: Crystal - 54.8 ^{0}C – nematic - 68.3 ^{0}C - isotropic, (ii) a binary mixture (MCB) of 70 wt% of 8OCB + 30 wt% of octyl cyanobiphenyl (8CB) with the phase transition sequence: smectic A - 57.8 ^{0}C nematic - 70 ^{0}C - isotropic and iii) binary mixtures of 6OCB and 8OCB with different molar compositions, which show re-entrant nematic phase.

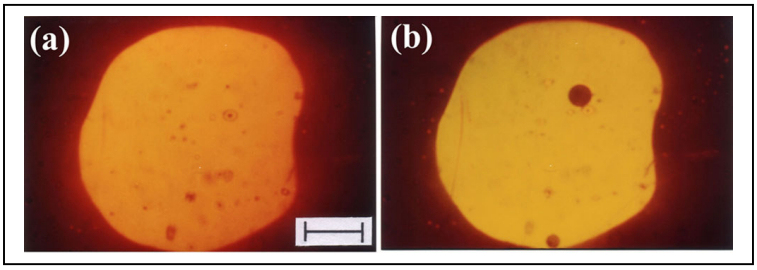

Figure 12: Photograph of a large drop of CBCC embedded in a glass matrix of sucrose between crossed polarisers set at 45^0 to the rubbing direction. The scale bar corresponds to 160 μm. (a) appearance of the drop before the formation of cavity and (b) after cavitation.

A photograph of a nematic drop of CBCC embedded in glassy sucrose matrix before the formation of cavity and after formation of cavity is shown in Figure 12. The temperature variation of $\Delta\mu$ under both isochoric as well as isobaric conditions are

shown in Figure 13. The $\Delta\mu$ data on a sample with cavity agrees well with the data on an independent isobaric measurement of the system at atmospheric pressure.

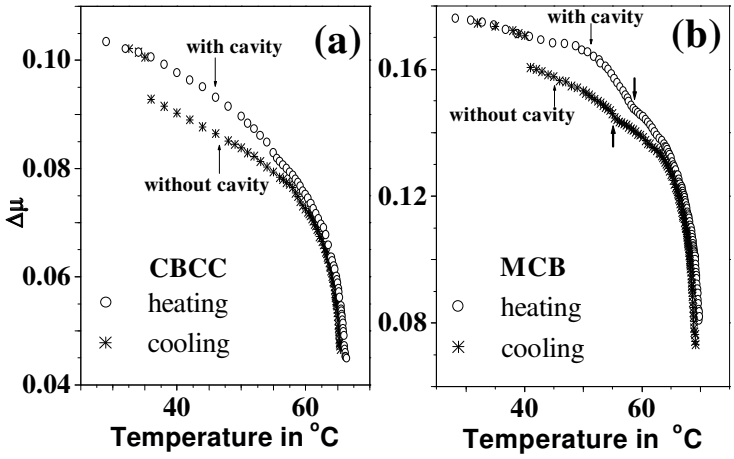

Figure 13: Temperature dependence of the birefringence $\Delta\mu$, measured (a) in the nematic phase of an embedded drop of CBCC (b) in the nematic as well as smectic phases of an embedded drop of MCB. In (b) the thick arrow indicates SmA-N transition. A jump in $\Delta\mu$ can be noticed in both the cases after the formation of cavity in the cooling mode.

The Freedericks threshold voltage for the splay deformation of the medium is given by $V_{th} = \pi\left[K_{11}/\varepsilon_o\Delta\varepsilon\right]^{1/2}$. K_{11} is the splay elastic constant, ε_0 is the vacuum dielectric constant, $\Delta\varepsilon$ is the dielectric anisotropy of the medium. We report the temperature variations of the threshold voltage V_{th} in the nematic phase of both CBCC and MCB under isochoric as well as isobaric conditions.

Using the values of dP/dT on MCB reported in chapter 5 the estimated *negative* pressure is ~230 bars at 40 ^{0}C at which the cavitation (formation of a vapour bubble) of MCB occurs in the smectic phase.

The Landau de Gennes model [3] is used to describe the NI transition. We have extended the LdG model, by taking into account the density-order parameter coupling. Comparison of isobaric and isochoric measurements allows us to estimate the coefficients coupling the order parameter and density of the extended LdG model.

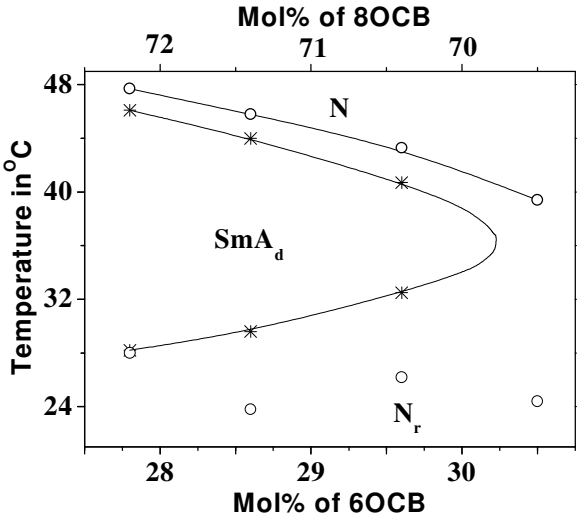

Figure 14: The concentration-temperature phase diagram of binary mixtures of 6OCB with 8OCB. ✳ corresponds to samples with cavity (isobaric condition). The N-SmA_d transition points of isochorically cooled samples fall on a smooth curve (upper circles). The lower circles represent the cavitation temperatures, at which transition from SmA_d phase under tension to N_r phase at normal pressure takes place.

The binary mixtures of 6OCB and 8OCB exhibit N-SmA_d-N_r phase sequence in a narrow range of concentrations of 6OCB. The P-T behaviour of the binary mixtures has been reported by Cladis et al [13]. The value of P_m, the maximum pressure up to which the SmA_d phase is stable decreases with increasing concentration of 6OCB [13]. The concentration-temperature phase diagram of the mixtures studied in droplets embedded in a sucrose glass matrix is shown in Figure 14. Under tension the thermal range of SmA_d widens. In fact in a region of concentration where there is no smectic phase in isobaric condition the smectic phase gets induced under tension as shown in the Figure 14.

Some of the results presented in this thesis have been published in the following references:

1. "Phase Transitions in Liquid Crystals Under Negative Pressures", V. Manjuladevi, R. Pratibha and N.V. Madhusudana, *Phys. Rev. Lett.* **88**, 55701, 4th Feb 2002.

2. "High pressure studies on a nematogen with highly polar molecules: evidence for a nematic-nematic transition", V. Manjuladevi and N. V. Madhusudana, *Curr. Sci.* **85**, 1056-1061, 2003.

3. "Liquid crystals under compression and tension", V. Manjuladevi and N. V. Madhusudana, (to appear in *SPIE proceedings*, special issue on XV Conference on Liquid Crystals: Chemistry, Physics and Applications, Zakopane, Poland, 2003).

The following papers are under preparation:

1. "Experimental studies on a binary mixture exhibiting a new type of Nematic-Nematic transition", V. Manjuladevi and N.V. Madhusudana.

2. "High pressure studies on some new types of liquid crystalline phase transitions", V. Manjuladevi and N.V. Madhusudana.

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