Chapter 4

Studies on the Termination of Smectic A- Smectic A Phase Boundaries
4.1 Introduction

The smectic A phase formed of nonpolar molecules is, as a rule, of monolayer type where the layer spacing $d$ is equal to the length of the molecule $l$. However, in molecules having strong polar end groups, several types of smectic A phases with different periodicities have been identified. Studies on such materials has led to many interesting results like smectic A polymorphism and re-entrant phenomena. This chapter presents dielectric and X-ray experiments conducted on such materials exhibiting different types of smectic A phases and in addition a re-entrant nematic phase. We begin here with a brief introduction to smectic A polymorphism, followed by a summary of the phenomenological model due to Prost and coworkers which provides a satisfactory explanation of these phenomena. Experimental results near a critical point are presented. Finally results obtained in a novel phase diagram are also discussed.

The chemical structure of a typical mesogen exhibiting monolayer smectic A phase (Sm $A_1$) is shown below. It consists of a central aromatic core which is

\[
\begin{align*}
R & \quad \text{-flexible alkyl chain} \\
X & \quad \text{-linkage group}
\end{align*}
\]

quite rigid with relatively flexible alkyl chain at one or both ends. Here $X$ is the
linkage group. If the chain at one end is replaced by a strongly polar group like e.g., CN, NO$_2$, it is now established that other types of smectic A phases can exist. Madhusudhana and Chandrasekhar$^1$ predicted theoretically that in such polar systems, minimisation of the free energy demands antiparallel association of neighbouring molecules. One consequence of this antiparallel near-neighbour correlation is the formation of a smectic layer, whose thickness ($d$) is greater than the length of the molecule ($l$). Leadbetter et al.$^2$ showed the existence of such a bilayer structure wherein the aromatic cores overlap in the middle of a layer and the alkyl chains extend outwards (see figure 4.1). An interesting feature of such a pair is that it is more symmetric than the individual molecule. Synthesis of these materials with a strong polar end group opened a new field of study, namely, smectic A polymorphism.

Sigaud et al.$^3$ for the first time identified a transition between two different smectic A phases in binary mixtures of DB5CN and TBBA (see figure 4.2). Later, X-ray studies by Hardouin et al.$^4$ revealed that the higher temperature smectic A phase is a monolayer smectic A (Sm $A_1$) with layer spacing ($d$) being approximately equal to the length of the molecule and the lower one bilayer smectic A (Sm $A_2$) with $d \approx 2l$. In this notation the smectic A phase exhibited by compounds like 8CB, is a partially bilayer smectic A phase (Sm $A_d$), where $1 < d < 2l$ (see figure 4.1). These phases can be identified from the X-ray scattering pattern of monodonrain samples. Figure 4.3a & b shows a schematic representation of the molecular arrangement along with the characteristic X-ray diffraction pattern for the different types of smectic A phases. The notable features in the X-ray diffraction pattern are
Studies on Sm A-Sm A phase boundaries

Figure 4.1: Schematic representation of the antiparallel arrangement in 8CB. (From Ref. 2).

Figure 4.2: Part of DB5CN/TBBA phase diagram showing Sm A₁-Sm A₂ transition. (From Ref. 3).
Figure 4.3: (a) Schematic representation of the molecular arrangement in Sm A₁, Sm A₂, and Sm A₃ phases. (b) The characteristic X-ray diffraction patterns for different types of smectic A phases. Here × denotes the direct beam, $q_z$ denotes the direction normal to the layer. Solid dot denotes condensed spot and the broad ring indicates a diffuse spot.
1. The monolayer Sm A\(_1\) phase shows a condensed peak at a wavevector \(2q_0 (=2\pi/l)\). In addition, a diffuse scattering centered around \(q_0' (=2\pi/l')\) where \(l < l' < 2l\) is also seen.

2. The partially bilayer Sm A\(_d\) shows a condensed spot at \(q_0'\), a weak second harmonic at \(2q_0'\) and a diffuse peak centered around \(2q_0\).

3. The Sm A\(_2\) phase shows condensed peaks at both \(q_0\) and \(2q_0\), with \(q_0\) as fundamental and \(2q_0\) as its second harmonic.

The occurrence of these polymorphic forms of smectic A phase is explained successfully by the phenomenological model introduced by Prost and coworkers.\(^5\)\(^-\)\(^7\) They used this model within the framework of the mean field theory to calculate the various theoretical phase diagrams\(^7\) which involve transitions between these different types of smectic A phases. In the next section a brief discussion of this model is given with particular emphasis on some of the phase diagrams predicted.

### 4.1.1 Phenomenological model

In this model the free energy of smectic A is expressed in terms of two order parameters, \(\rho(r)\) describing the mass density order parameter, and \(P_z(r)\), the dipolar order parameter associated with antiferroelectric ordering of the neighbouring molecules, along the z-axis. For Sm A\(_1\), \(P_z(r) = 0\), whereas, for Sm A\(_2\) phase both \(\rho(r)\) and \(P_z(r) \neq 0\). The competition between these two types of orders trying to condense at two incommensurate length scales leads to different
Studies on \textit{Sm A-Sm A phase boundaries} 59

types of smectic A phases. Another offshoot of this feature is the re-entrant phenomena which we will not discuss here.

To describe the appearance of modulated order, order parameters $\rho(r)$ and $P_2(r)$ are rewritten as,

\begin{align*}
P_2(r) &= \operatorname{Re}[\psi_1(r)] \\
\rho(r) &= \operatorname{Re}[\psi_2(r)]
\end{align*}

(4.1)

where $\psi_1(r)$ and $\psi_2(r)$ are complex fields:

\begin{align*}
\psi_1(r) &= \psi_1 e^{iq_1 r} \\
\psi_2(r) &= \psi_2 e^{iq_2 r}
\end{align*}

(4.2)

In terms of these fields, the Landau-Ginzburg free energy in d-dimension in excess of the nematic free energy is

\begin{align*}
\Delta F &= \int d^d r \left[ \frac{1}{2} r_1 |\psi_1|^2 + \frac{1}{2} D_1 (\Delta + k_1^2) |\psi_1|^2 + \frac{1}{2} C_1 |\nabla_\perp \psi_1|^2 \\
&\quad + \frac{1}{2} r_2 |\psi_2|^2 + \frac{1}{2} D_2 (\Delta + k_2^2) |\psi_2|^2 + \frac{1}{2} C_2 |\nabla_\perp \psi_2|^2 + u_1 |\psi_1|^4 \\
&\quad + u_2 |\psi_2|^4 + 2u_{12} |\psi_1|^2 |\psi_2|^2 - w \operatorname{Re} \overline{\psi_1^2 \psi_2^*} \right]
\end{align*}

(4.3)

where $r_1 = a_1(T - T_{1c})$ and $r_2 = a_2(T - T_{2c})$ measure the temperature from the non-interacting mean field transition temperatures $T_{1c}$ and $T_{2c}$ of the fields $\psi_1$ and $\psi_2$. $\nabla_\perp$ is a derivative in the plane perpendicular to the z-axis, parallel to $\vec{n}$. The elastic term $|\Delta^2 + k_1^2| \psi_1|^2$ and $|\Delta^2 + k_2^2| \psi_2|^2$ in equation 4.3 favour $q_1^2 = k_1^2$ and $q_2^2 = k_2^2$. The term $\operatorname{Re} \overline{\psi_1^2 \psi_2^*}$ favours lock-in at $q_\rho = 2q_\rho$.

This free energy leads to the following phases.

1. nematic phase with $|\psi_1| = |\psi_2| = 0$

2. Sm A$_1$ phase with $|\psi_1| = 0$, $|\psi_2| \neq 0$, $q_\rho = k_2$ and
Studies on Sm A-Sm A phase boundaries

3. Sm A$_2$ phase with $|\psi_1| \neq 0$, $|\psi_2| \neq 0$ and $q_\rho = \frac{1}{2} q_\rho = q_o$

Note that an antiferroelectric smectic A phase with no long range mass density modulation ($|\psi_1| \neq 0$, $|\psi_2| = 0$) is never stable because a non-zero $|\psi_1|$ always generates a non-zero $|\psi_2|$ via the third order terms in $\Delta F_s$.

For Sm A$_1$ phase the free energy density is obtained by minimizing

$$F_{Sm A_1} = \frac{1}{2} r_2 |\psi_2|^2 + u_2 |\psi_2|^4$$

(4.4)

with respect to $|\psi_2|$. 

The free energy density for the bilayer Sm A$_2$ phase is obtained by minimizing

$$F_{Sm A_2}(|\psi_1|, |\psi_2|, q_o) = \frac{1}{2} \left[ r_1 + D_1 (q_o^2 - k_1^2) \right] |\psi_1|^2 + \frac{1}{2} \left[ r_2 + D_2 (4q_o^2 - k_2^2) \right] |\psi_2|^2$$

$$- w |\psi_1|^2 |\psi_2| + u_1 |\psi_1|^4 + u_2 |\psi_2|^4 + 2u_{12} |\psi_1|^2 |\psi_2|^2$$

(4.5)

with respect to $|\psi_1|, |\psi_2|$ and $q_o$.

To proceed further they introduced rescaled variables

$$\psi_1 = \frac{w}{u_{12}} \sqrt{\frac{D_2}{D_1}} x \cos \theta$$

(4.6)

$$\psi_2 = \frac{w}{2 u_{12}} x \sin \theta$$

(4.7)

so that

$$q_o^2 = k_1^2 \cos^2 \theta + \frac{1}{4} k_2^2 \sin^2 \theta$$

(4.8)

where $x$ measures the degree of order and $\theta$ the relative amplitudes of $\psi_1$ and $\psi_2$. In terms of these variables the free energy density becomes,

$$f(x, \theta) = x^2 (y_1 \cos^2 \theta + y_2 \sin^2 \theta + z^2 \cos^2 \theta \sin^2 \theta) - 2x^3 \cos^2 \theta \sin \theta$$

$$+ x^4 (1 + \partial u_1 \cos^4 \theta + \partial u_2 \sin^4 \theta)$$

(4.9)
Studies on Sm A - Sm A phase boundaries

where,

\[ y_1 = 2 \frac{u_{12}}{w_2 r_1}, \quad y_2 = \frac{1}{8} \frac{D_1 u_{12}}{D_2 w_2 r_2} \]

\[ z^2 = \frac{2 D_1 u_{12}}{w^2} \left( k_1^2 - \frac{1}{4} k_2^2 \right)^2 \]

\[
\partial u_1 = 16 \frac{u_1 D_2}{u_{12} D_1} - 1, \quad \partial u_2 = \frac{1}{16} \frac{u_2 D_1}{u_{12} D_2} - 1
\] (4.10)

where \( y_1 \) and \( y_2 \) are the temperature variables, and \( z^2 \) is the incommensurability parameter measuring the degree of mismatch between \( k_1 \) and \( k_2/2 \). The usual stability requirements on fourth order terms require \( \partial u_1, \partial u_2 \) to be greater than -1. Numerical calculations performed by Barois et al.\(^7\) to minimize the free energy have led to a variety of phase diagrams. Only the relevant phase diagrams are discussed here.

4.1.2 Phase Diagrams

Case 1

For small incommensurability parameter \( z^2 \) and symmetric elastic and fourth order terms (\( \partial u_1 = \partial u_2 \)) the phase diagram is shown in figure 4.4. The special features of this diagram are (1) Nematic-Sm A\(_1\) boundary is second order throughout and terminates at a critical end point \( Q \) where N, Sm A\(_1\), Sm A\(_2\) phases meet. (2) There are two tricritical points, viz., R on Sm A\(_1\)-Sm A\(_2\) and P on the N-Sm A\(_2\) boundary.
Studies on Sm A-Sm A phase boundaries

Figure 4.4: Phase diagram in the $y_1 - y_2$ plane for small incommensurability parameter $z^2 = 0.25$, and the potentials $\partial u_1 = \partial u_2 = 0$. Solid (or dashed) line correspond to first (or second) order transition. Here Q is a critical end point, P and R are tricritical points. (From Ref. 7).

Figure 4.5: Phase diagram for $z^2 = 0.25$ with asymmetric potentials $\partial u_1 = 6, \partial u_2 = -0.857$. Solid (or dashed) line correspond to first (or second) order transition. Notice that the first order Sm A$_2$-Sm A'$_2$ (or Sm A$_d$) phase boundary ends up at a critical point C followed by a continuous evolution region. (From Ref. 7)
Studies on Sm A-Sm A phase boundaries

**Case 2**

If the elastic constants $D_1$ and $D_2$ are different and favour an easy compression of $\psi_1$ (i.e., $\partial u_1$ increases and $\partial u_2$ decreases), then, at small values of $z^2$, a new first order phase boundary separating two smectic A$_2$ phases appears (see figure 4.5). The two smectic A$_2$ phases are distinguished by different values of $\theta$ and from equation 4.8 different values of $q_\psi$. For small $\theta$, $q_\psi$ is of the order of $k_1$, and $\psi_1$ is much larger than $\psi_2$. Hence the Sm A'$_2$ can be identified with the experimentally observed Sm A$_d$ phase even though $\psi_2$ is strictly speaking non-zero.

For $0 < \theta < \pi/2$, the amplitudes of $\psi_1$ and $\psi_2$ are comparable leading to the Sm A$_2$ phase. The discontinuities in $q_\phi^2$ and $\sin^2 \theta$ across the new phase boundary are

$$\Delta q_\phi^2 = \left( \frac{k_2^2}{4} - k_1^2 \right) \Delta (\sin^2 \theta) \quad (4.11)$$

The new phase boundary is tangent to the first order N-Sm A$_2$ line at P and terminates at a critical point C where $\Delta q_\phi^2$ goes to zero. In the framework of mean field theory critical fluctuations in the vicinity of C are expected to be similar to those encountered at the liquid-gas critical point. The presence of the critical point C indicates, as expected, that there is no difference in symmetry between the Sm A$_2$ and Sm A'$_2$ (or Sm A$_d$) phase with different relative amplitudes of $\psi_1$ and $\psi_2$.

Thus we see here that competition between ordering at two different length scales results in the formation of the three phases Sm A$_1$, Sm A$_d$ and Sm A$_2$. These phases have the same macroscopic symmetry (i.e., one dimensional mass density wave along the optic axis or the layer-normal) but differ from each other.
only in the values of d. It is possible to go from Sm $A_1$ to Sm $A_d$ or from Sm $A_d$ to Sm $A_2$ phase merely by a continuous variation the layer spacing d. First order transitions in which there is discontinuous change in the wave vector $q_0$ (i.e., Sm $A_1$-Sm $A_d$ or Sm $A_d$-Sm $A_2$ transition) are always possible. A line of such first order transitions may terminate at a critical point where the difference in wave vector between the two phases goes to zero. Such a critical point provides a continuous path coexisting between Sm $A_1$ (or Sm $A_2$) and Sm $A_d$ phases. But the situation is different for Sm $A_1$-Sm $A_2$ transition. It can be either first order or second order. The latter is due to the exact doubling of the layer periodicity.

This chapter discusses two important results, namely,

1. Precise dielectric measurement near the Sm $A_d$-Sm $A_2$ critical point in a binary liquid crystalline system.

2. The existence of a continuous thermodynamic path between Sm $A_1$ and Sm $A_2$ phases.

### 4.2 The Sm $A_d$ - Sm $A_2$ critical point

The first experimental observation of the Sm $A_d$-Sm $A_2$ critical point was in a binary system of 4-n-undecyloxyphenyl-$4'$-($4''$-cyanobenzyloxy) benzoate (or 11OPCBOB) and 4-n-nonyloxybiphenyl-$4'$-cyano benzoate (or 9OBCB), employing high resolution X-ray techniques. Subsequently, high resolution calorimetric studies were conducted on the same system which confirmed the conclusions arrived at from the X-ray studies. Results of these experiments performed by Shashidhar et al is shown in figure 4.6. It is observed that the strength of
Figure 4.6: Plots of wave vector $q$, $q'$ vs. temperature ($T$) for different mixtures of 11OPCBOB in 9OBCB. The mole-fraction ($X$) of 11OPCBOB in the mixture are a) 0.55, b) 0.571, c) 0.597, d) 0.619, e) 0.642, f) 0.715, g) 0.8 and h) 1.0. The corresponding temperature scales are identified. For $X < 0.642$ (plots a-d), first order Sm $A_2$-Sm $A_2$ transition is seen which manifests as a jump in the wavevector. The data in the two phase region are shown with filled circles, while the dashed line represent the width of two phase region. The critical point CP is identified by the vertical inflection point seen for $X = 0.642$ (plot e). (From Ref. 9).
the first order transition, characterised by a two-phase coexistence region and an accompanying jump in wave vector, decreases with increasing concentration, vanishes to zero at \( X=0.642 \), beyond which the wave vector varies continuously between the two phases.

Since the constituent molecules are polar and the extent of interdigitation of molecules in the neighbouring layers vary from one phase to another, one can expect the changes to be reflected in dielectric measurements also. In fact, earlier dielectric studies on materials having different smectic \( A \) phases have shown this to be true.\(^{11-14} \) We present here precise dielectric measurements on the same binary system, viz., 11OPCBOB and 9OBCB, which again reveal the critical point in a striking fashion.

### 4.2.1 Experimental

The structural formulae and transition temperatures of 11OPCBOB and 9OBCB\(^{15} \) are given in Table 4.1.

**Dielectric setup**

Dielectric experiments were conducted using a setup that was available in the laboratory.\(^{12} \) A schematic diagram of the cell and the heater assembly is shown in the figure 4.7. The cell is made of two aluminium coated glass plates which serve as electrodes. The thickness of the cell is defined by a mylar spacer (thickness \( \approx 25 \mu \)). The samples were filled in the isotropic phase by capillary action. The cell is held rigidly inside a copper frame with the help of a rectangular
Studies on Sm A-Sm A phase boundaries

**11OPCBOB**

\[
\text{C}_{11}\text{H}_{23}\text{O} \quad \text{OOC} \quad \text{OCH}_2 \quad \text{CN}
\]

4-n-undecyloxyphenyl - 4′-(4″-cyanobenzyloxy) benzoate

Isotropic \(\rightarrow\) N \(\rightarrow\) Sm \(\rightarrow\) Sm \(\rightarrow\) K

153.3 \(\rightarrow\) 154.5 \(\rightarrow\) 106

**90 BCB**

\[
\text{C}_9\text{H}_{19}\text{O} \quad \text{OOC} \quad \text{CN}
\]

4-n-nonyloxybiphenyl - 4′-cyanobenzoate

Isotropic \(\rightarrow\) N \(\rightarrow\) Sm \(\rightarrow\) Sm \(\rightarrow\) K

228.3 \(\rightarrow\) 207.8 \(\rightarrow\) 112.6

**Table 4.1:** Structural formulae and transition temperatures (in °C) of 11OPCBOB & 90BCB.
'G' clamp. Electrical contacts are made with the extended area of the glass plates. This cell assembly was positioned inside the central part of the heater. Nichrome tape wound on the top and bottom side of the heater assembly facilitated temperature control of the cell. The heater assembly was covered with hylum sheets for good thermal insulation. The assembly was mounted on a rotatable stage enabling positioning of the sample for measurements of both parallel and perpendicular components of the dielectric constants. The temperature of the sample was measured with the help of chromel-constantan thermocouple in conjunction with a low drift digital nanovoltmeter (Keithley, Model 181). The samples were aligned by cooling slowly (2-3° C/hour) from the nematic phase in the presence of a 2.4T magnetic field provided by an electromagnet (Bruker B-E 25). The capacitance of the cell is measured using a variable frequency Impedance Analyser[HP 4192A]. This instrument can be used to measure eleven impedance associated parameters such as capacitance C, conductance G, susceptance B, Dissipation or dielectric loss factor D, etc., with a basic accuracy of 0.1% throughout the range of measurement. The oscillating or measuring voltage is kept at 1 V rms. The principle of capacitance measurement is based on vector-voltage-current ratio measurement method. The capacitance measuring range is 0.1 pF to 100 nF and that of the dielectric loss factor is 0.0001 to 19.999. Experiments were done in the four probe configuration which eliminates errors due to residual impedance of test leads. The dielectric constant of the sample is given by the ratio of capacitance of the sample to that of an empty cell.

The block diagram of the experimental setup used is shown in figure 4.8. Both the temperature measuring digital multimeter (Keithley 181) and the
Studies on Sm A-Sm A phase boundaries

Figure 4.8: Block diagram of the experimental setup.
impedance analyser (HP4192A) were interfaced with a micro-computer (HP86B) through HPIB (IEEE 488) bus for data acquisition and storage purpose. The static dielectric constants, $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$, parallel and perpendicular to the director respectively were measured at 10kHz, a frequency which is well below the relaxation frequency of any mode in the system, by varying the temperature of the sample at a uniform rate of 4-5°C/hour across the transition. Dispersion measurements were done by stabilising the sample temperature at a particular value and the frequency was swept from 1kHz to 13 MHz at a desired step value.

4.2.2 Results and Discussion

The temperature-concentration (T-X) phase diagram of 11OPCBOB:9OBCB system obtained by Shashidhar et al., is shown in the figure 4.9. Here X is the mol fraction of 11OPCBOB in in the mixture. From the phase diagram it is seen that for $X<0.52$ the ribbon phase Sm $\tilde{C}$ intervenes between Sm $A_d$ and Sm $A_2$ phases. (Sm $\tilde{C}$ is an antiphase. In this phase the local order is tilted-Sm $A_2$ like but the direction of dipolar heads alternates periodically within a layer and this results in a rectangular symmetry). However, with increasing X, Sm $\tilde{C}$ is suppressed, leading to a direct Sm $A_d$-Sm $A_2$ transition. This first order Sm $A_d$-Sm $A_2$ phase boundary then terminates at a critical point followed by continuous evolution region.

Static dielectric constant measurements were done on 8 mixtures and the pure compound 11OPCBOB. Figures 4.10-4.18 show the thermal variation of $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ in the Sm $A_d$ and Sm $A_2$ phases for $X=0.55$, 0.59, 0.63, 0.65, 0.68,
Studies on Sm A-Sm A phase boundaries

Figure 4.9: Temperature-concentration (T-X) phase diagram for the binary mixture of 11OPCBOB in 9OBCB. X is the mole fraction of 11OPCBOB in the mixture. First order Sm A\textsubscript{d}-Sm A\textsubscript{2} transition terminates at the critical point (CP). Inset shows the phase diagram in the vicinity of CP on an enlarged scale. K → crystal, N → nematic, I → isotropic, Sm Ĉ → antiphase Sm Ĉ, Sm C\textsubscript{2} → bilayer Sm C\textsubscript{2} phase. (From Ref. 9).
Figure 4.10: Temperature variation of $\epsilon_\parallel$ and $\epsilon_\perp$ for $X=0.55$.

Figure 4.11: Thermal variation of $\epsilon_\parallel$ and $\epsilon_\perp$ for $X=0.59$. 
Figure 4.12: Thermal variation of $\epsilon_1$ and $\epsilon_2$ for $X=0.63$.

Figure 4.13: Temperature variation of $\epsilon_1$ and $\epsilon_2$ for $X=0.65$. 
Figure 16: Thermal variation of $\epsilon_\parallel$ and $\epsilon_\perp$ for $X=0.80$.

Figure 17: Thermal variation of $\epsilon_\parallel$ and $\epsilon_\perp$ for $X=0.90$. 
Figure 4.18: Thermal variation of $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ for $X=1.00$ or 11OPCBOB.
Studies on Sm A-Sm A phase boundaries

0.72, 0.80, 0.9 and for pure 11OPCBOB respectively. For concentrations below \( X \leq 0.65 \), both \( \epsilon_\parallel \) and \( \epsilon_\perp \) show a steep variation across the transition, whereas for higher concentrations this variation is much smoother. As mentioned earlier X-ray studies\(^9\) identified \( X=0.642 \) as the critical point concentration. Thus there is a first order transition for \( X < 0.642 \) and a continuous evolution type without a phase transition for \( X > 0.642 \). The change in the nature of the transformation manifests as a change in the steepness of the thermal variation of both \( \epsilon_\parallel \) and \( \epsilon_\perp \). Another point to be noted here is that there is a cross-over in the values of \( \epsilon_\parallel \) and \( \epsilon_\perp \) near the transition. Plots of dielectric anisotropy \( (\Delta \epsilon = \epsilon_\parallel - \epsilon_\perp) \) versus temperature for different concentrations are shown in figures 4.19-4.27. Although the steepness of the \( \Delta \epsilon \) variation near the transition shows a concentration dependence, it was not significant enough to locate the critical point accurately.

In order to locate the critical point we proceeded as follows. The data of \( \Delta \epsilon \) versus temperature was fitted to an expression of the form

\[
\Delta \epsilon = A^z t^B + C(T - T_c) + D
\]

(4.12)

where \( t = \frac{T - T_c}{T_c} \) is the reduced temperature and \( C(T - T_c) \) represents the background contribution to \( \Delta \epsilon \). D is the value of \( \Delta \epsilon \) at \( T_c \). A non-linear least square fit with all the parameters floating, was performed using the Marquardt algorithm.

It may be noted that a theoretical one-loop model\(^8\) predicts a similar expression for the variation of specific heat. Equation 4.12 describes the data very well for all the mixtures studied. Figure 4.28 shows representative plots of the data for \( X = 0.55, 0.63 \) & 0.72 along with the fit to equation 4.12. For comparison,
Figure 19: Thermal variation of dielectric anisotropy $\Delta \varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp}$ for $X=0.55$.

Figure 20: Thermal variation of $\Delta \varepsilon$ for $X=0.59$. 
Figure 21: Temperature variation of $\Delta \epsilon$ for $X=0.63$.  

Figure 22: Temperature variation of $\Delta \epsilon$ for $X=0.65$.  

\[ X = 0.65 \]
\[ X = 0.63 \]
Figure 23: Thermal variation of $\Delta \epsilon$ for $X=0.68$.

Figure 24: Thermal variation of $\Delta \epsilon$ for $X=0.72$. 

Figure 25: Thermal variation of $\Delta \epsilon$ for $X=0.80$.
Figure 26: Thermal variation of $\Delta \epsilon$ for $X=0.90$. 
Figure 4.27: Thermal variation of $\Delta\epsilon$ for $X=1.00$, i.e., pure 11OPCBOB.
Figure 4.28: Representative plot showing fit to equation 4.12 for $X = 0.55$, 0.63 and 0.72.
Circles represent measured data points and solid line the fitting.
the X-ray data for $X=0.642$ for which a similar kind of fit was done by Jeong et al. is reproduced in the figure 4.29.

Figure 4.30 shows the thermal variation of $\frac{d}{dT}(\Delta \epsilon)$ calculated using the fit parameters $A^\pm , B, C$ & D for different concentration. The salient features observed are as follows:

1. the peaks resemble very closely to the specific heat curves obtained near the critical point.
2. The height of the peak is much larger and narrow for $X=0.63$ than for $X<0.63$ or $X>0.63$.

The peak heights obtained in this manner are plotted as a function of concentration in figure 4.31. It is seen that the peak height increases from either side (lower as well as higher concentrations) and reaches a maximum for $X=0.64$. We identify this concentration for which peak height attains a maximum as the critical point concentration. The critical point concentration $X_c=0.64$, obtained in this way, is in excellent agreement with the value obtained from both X-ray and calorimetric measurements.

### 4.2.3 Dispersion Studies

Dispersion measurements (parallel to the director) were carried out on $X=0.63$, (a concentration with a first order Sm $A_d$-Sm $A_2$ transition) to see whether there is a jump in the relaxation frequency $f_R$ at the transition.

The measurements of frequency dependent dielectric constant ($\epsilon(\omega)$), with
Figure 4.29: Fitting of the smectic layer spacing $d$ to an expression similar to equation 4.12. (From Jeong et al\textsuperscript{10}).
Figure 4.30: Plot of $\frac{d}{dT}(\Delta \epsilon)$ as a function of reduced temperature $T - T_{\text{peak}}$ for different concentrations. For the sake of presentation, the data lying within 0.5°C of $T_{\text{peak}}$ is shown.
Studies on Sm A-Sm A phase boundaries

Figure 4.31: Top panel: Peak height of $\frac{d}{dT}(\Delta \epsilon)$ vs. T-T$_{peak}$ curves, plotted as a function of X. Notice that $\left[\frac{d}{dT}(\Delta \epsilon)\right]_{peak}$ increases on moving from both X<0.64 and X>0.64 and reaches a maximum for X=0.64. Bottom panel: Partial T-X phase diagram of the binary system 110PCBOB and 90BCB. Solid line denote the Sm $A_d$-Sm $A_2$ transition boundary while the dashed line represent the locus of "inflection point" in the supercritical region. • → denotes the critical point estimated from peak height plots of $\frac{d}{dT}(\Delta \epsilon)$ curves.
$w = 2\pi \times \text{frequency}$ were done by recording the capacitance and dissipation factor $D$ while sweeping the frequency from 1kHz to 10MHz at a desired step value. Care was taken to collect more data in the neighbourhood of the relaxation frequency. During this dispersion scan the temperature was maintained constant to within ±10mK. The real part of the dielectric constant $\epsilon'$ is given by the ratio of capacitance of the sample to that of an empty cell, while the imaginary part $\epsilon''$ is the product of $\epsilon'$ and D. The frequency dependence of the complex dielectric constant $\epsilon^*(\omega)$ is given by

$$\epsilon^*(\omega) = \epsilon' - j\epsilon'' = \epsilon_\infty + \frac{\Delta \epsilon}{(1 + j\omega\tau)^{1-h}}$$  \hspace{1cm} (4.13)$$

where $\Delta \epsilon = \epsilon_0 - \epsilon_\infty$ is the dielectric strength, $\epsilon_0$ & $\epsilon_\infty$ are the values of dielectric constant at frequencies far below and far above $f_R$ respectively, $\tau = 1/(2\pi f_R)$ the relaxation time, and $h$ is a constant called the distribution parameter with $0 \leq h < 1$. When $h=0$ equation 4.13 reduces to a pure Debye type of relaxation.

Rationalising equation 4.13

$$\epsilon' = \epsilon_\infty + \frac{\Delta \epsilon}{1 + (\omega\tau)^{2(1-h)}} \sin(\pi h/2)$$  \hspace{1cm} (4.14)$$

$$\epsilon'' = \frac{\Delta \epsilon (\omega\tau)^{1-h} \cos(\pi h/2)}{1 + (\omega\tau)^{2(1-h)}}$$  \hspace{1cm} (4.15)$$

Real ($\epsilon'$) and imaginary ($\epsilon''$) parts of the dielectric constant has been fitted to equation 4.14 & 4.15 respectively to obtain the dielectric strength $\Delta \epsilon$, the relaxation frequency $f_R$, $\epsilon_\infty$ and $h$. The fitting has been carried out using a non-linear least-square program based on the Marquardt algorithm by floating all the parameters involved.
Studies on Sm A-Sm A phase boundaries.

Expressions 4.14 & 4.15 describe the data very well over the entire range of measurement. Further the distribution parameter \( h \) came out to be quite small (\( \sim 0.05 \)) indicating that the relaxation process is a 'pure Debye type. Representative loss curve (semi-log plot of \( e'' \) versus frequency) and Cole-cole plots (plot of \( e' \) & \( e'' \)) at \( T_c = -5.86^\circ C \), i.e., in the Sm A\(_2\) phase are shown in figure 4.32. Also shown are the fitting obtained for the expression 4.14 & 4.15. Similar type of plots in the Sm A\(_d\) phase (\( T_c + 5.9^\circ C \)) and at a temperature close to \( T_c (T_c - 0.1^\circ C) \) are shown in figures 4.33 & 4.34.

Figure 4.35 shows a plot of \( f_R \) obtained in this way versus \( 1/T \) for \( X=0.63 \). The results show that there is a slight increase in the \( f_R \) value on passing from Sm A\(_d\) to the Sm A\(_2\) phase. The activation energy, \( W \) for the relaxation process can be evaluated using the expression

\[
f_R \propto e^{-W/kT}
\]

where \( k \) is the Boltzmann constant. The values \( W \) calculated from the linear portion of the \( f_R \) versus \( 1/T \) plot in the Sm A\(_d\) and Sm A\(_2\) phases are \( W_{Sm A_d} = 0.39eV \) & \( W_{Sm A_2} = 0.46eV \). This type of difference has been observed earlier also on a different material showing a Sm A\(_d\)-Sm A\(_2\) transition.\(^{12,14}\) The fact that \( W_{Sm A_2} > W_{Sm A_d} \) has been suggested to be indicative of a better packing of molecules in bilayer Sm A\(_2\) phase.

### 4.2.4 Nature of the Sm A\(_d\)-Sm A\(_2\) critical point

The theory of Barois et al.,\(^7\) mentioned in section 4.1.1 is a mean field one. More recently, Park et al.,\(^8\) developed a nonlinear elastic model to describe the Sm A\(_d\)-
Figure 4.32: Top panel: Plot of $\varepsilon''$ vs. frequency (dielectric loss curve). Solid line is a fitting to equation 4.14. Bottom panel: Plot of $\varepsilon''$ vs. $\varepsilon'$ plot (Cole-Cole plot) in the Sm A$_2$ phase ($T-T_c = -5.86^\circ$C). Solid line is a fitting to equation 4.15.
Figure 4.33: Top panel: Dielectric loss curve in the Sm\textsubscript{A\textsubscript{2}} phase ($T - T_{c} = -0.1^\circ$C) near the Sm\textsubscript{A\textsubscript{2}}-Sm\textsubscript{A\textsubscript{2}} transition. Solid line is a fitting to equation 4.14. Bottom panel: Corresponding Cole-Cole plot in the Sm\textsubscript{A\textsubscript{2}} phase. Solid line is a fitting to equation 4.15.
Studies on Sm A-Sm A phase boundaries

Figure 4.34: Top panel: Dielectric loss curve in the Sm $\text{A}_d$ phase. ($T-T_c = +5.93^\circ\text{C}$). Solid line is a fitting to equation 4.14. Bottom panel: Corresponding Cole-Cole plot in the Sm $\text{A}_d$ phase. Solid line is a fitting to equation 4.15.
Studies on Sm A-Sm A phase boundaries

Figure 4.35: $f_R$ vs. $1/T$ plot for $X=0.63$. 

$1 \div T \times 10^{-4} (K^{-1})$
Studies on Sm A–Sm A phase boundaries

Sm A₂ critical point by taking into account fluctuations in the layer thickness. This theory predicts that the Sm A₄–Sm A₂ critical point should belong to a new universality class with d_u, the upper critical dimension, being six. (The upper critical dimension is defined as that dimension above which the system should exhibit mean field behaviour). The theory also predicts that the layer compressional elastic constant B vanishes at the critical point in exact analogy with the divergence of the bulk compressibility at the liquid-gas critical point. The specific heat at constant pressure and B along the critical pressure line should yield the exponent \( \nu/\Delta \). On the other hand specific heat at constant layer spacing is expected to yield the exponent \( \alpha \). However, it has also been shown that the upper critical dimension of the Sm A₄–Sm A₂ critical point drops to 2.5 when the splay-type critical fluctuations are suppressed by either a magnetic field or a local strain field.

Heat capacity measurement across Sm A₄–Sm A₂ critical point (in the same binary system as in our study i.e., 11OPCBOB and 9OBCB) by Jeong et al. attempted to verify these theoretical predictions. The variation of specific heat in two near-critical mixtures with \( X=0.641 \) and 0.655 (X is the mole fraction of 11OPCBOB) are characterized by the critical exponent \( \nu/\Delta = 0.6 \pm 0.2 \). Smectic layer thickness for \( X=0.642 \) varied with an exponent \( \nu/\Delta = 0.62 \). The compressional-elastic-modulus(B) for \( X=0.67 \) (in the same binary system) varied with an exponent \( \nu/\Delta = 0.4 \pm 0.01 \). Wen et al. did calorimetric measurements across Sm A₄–Sm A₂ critical point in mixtures of 11OPCBOB and its lower homologue 10OPCBOB. The variation of the heat capacity for three near-critical mixtures could be described by a simple power law with a critical exponent \( \nu/\Delta = 0.45 \pm 0.08 \). These experimental exponent
values, which are different from 3D-Ising model \((\nu/\Delta = 0.79)\) or the mean-field approximation \((\nu/\Delta = 0.67)\), support the theoretical prediction that the Sm A\(_d\)-Sm A\(_2\) critical point belongs to a new universality class.

### 4.3 Continuous thermodynamic path between three smectic A phases of the same symmetry

The phase transition between the three polymorphic forms of smectic A phases, namely, Sm A\(_1\), Sm A\(_d\), Sm A\(_2\), differing from each other only by the wavelength of their periodic modulations, are of considerable interest since all of them have the same macroscopic symmetry. As discussed in the previous sections of this chapter, there can only be a first order phase transition between Sm A\(_d\) and Sm A\(_2\) as well as between Sm A\(_d\) and Sm A\(_1\). Also it is seen both theoretically\(^7,8\) and experimentally\(^9-10,19-20\) that first order Sm A\(_d\)-Sm A\(_2\) phase boundary terminates at a critical point beyond which Sm A\(_d\) phase evolves continuously into Sm A\(_2\).

In the case of Sm A\(_d\)-Sm A\(_1\) transition, two different situations have been dealt with theoretically\(^21\). In the mean field limit, the theory predicts the existence of a Sm A\(_d\)-Sm A\(_1\) critical point similar to the Sm A\(_d\)-Sm A\(_2\) critical point. However, when the effect of fluctuations is considered the theory predicts that the Sm A\(_d\)-Sm A\(_1\) boundary can end either as a critical point or in a nematic island. The theory also predicts several interesting results for the nematic island (see figure 4.36). The existence of two distinct critical endpoints (the points at which a second order line meets two first order boundaries) \(a\) & \(b\) on the
Studies on Sm A-SmA phase boundaries

Figure 4.36: Theoretical phase diagram predicted by the dislocation-loop theory of Prost and Toner, showing the nematic island at the terminus of the SmA–SmA1 phase boundary. There are two types of nematics in this island, viz., N_d and N_1. c is the critical point at which a first order N_d-N_1 transition ends. a & b are critical end points for the N_1-SmA1 and N_d-SmA_d boundaries respectively. This nematic island is seen separated from the main domain nematic region. (From Ref.21).
Studies on Sm A-Sm A phase boundaries

continuous smectic A-nematic line which bounds the island, the first order line \((bc)\) which separates two different types of nematic phases, \(N_d\) and \(N_1\), and the termination of \(N_d-N_1\) boundary at the critical point \(c\) (Figure 4.36). Prost and Toner\(^2\) have also worked out a variety of possible phase diagrams that are consistent with the theory. Experimentally,\(^{22-24}\) the closed-loop nematic domain at the termination of the first-order \(\text{Sm } A_d-\text{Sm } A_1\) boundary as well as continuous evolutions between \(\text{Sm } A_d\) and \(\text{Sm } A_1\) have been observed.

The \(\text{Sm } A_1-\text{Sm } A_2\) transition, which was the first observed smectic A-smectic A transition\(^3\) can either be second order or first order. The former is due to the exact doubling of the layer periodicity at the transition.

To our knowledge, both theoretically calculated\(^5-8\) as well as experimentally observed\(^3,25\) phase diagrams have always involved phase transitions (either first order or second order) on going from \(\text{Sm } A_1\) to \(\text{Sm } A_2\). However, the theoretical phase diagram (see figure 4.37) proposed by Park et al.,\(^8\) showed the possibility of a continuous path between \(\text{Sm } A_1\) and \(\text{Sm } A_2\) via \(\text{Sm } A_d\) phase. Experimentally such a continuous path has not been observed. The remaining part of this chapter discusses a novel result which shows the observation of continuous thermodynamic path between \(\text{Sm } A_1\) and \(\text{Sm } A_2\) phases. X-ray and optical studies show that this path, observed in a temperature-concentration diagram of binary liquid-crystal system, follows a continuous evolution from \(\text{Sm } A_1\) to \(\text{Sm } A_2\) via the \(\text{Sm } A_d\) phase.
Figure 4.37: Possible phase diagram with different smectic A phases showing a second order Sm A1-Sm A2 line(BT), a tricritical point(T) and a first order Sm A1-Sm Ad line(TC) terminating in a critical point C. The paths indicated by the numbered arrows correspond to (1) continuous passage from Sm A2 to Sm Ad, (2) continuous passage between two Sm Ad phases of different layerspacings, (3) continuous passage from Sm Ad to Sm A1, (4) a second order Sm A1 to Sm A2 transition and (5) & (6) first order Sm A1 to Sm Ad transitions. (3) also shows possibility of a continuous path between Sm A2 to Sm A1 phases. (From Ref.8).
4.3.1 Experimental

Compounds used

The compounds used are 4-n-decyloxy-(4'-isothiocyanatopheny1)- benzoate or 10. O. NCS and 11OPCBOB. The compound 10.O.NCS shows the Sm A\textsubscript{1} phase while 11OPCBOB shows, as mentioned already, a continuous evolution from Sm A\textsubscript{d} to Sm A\textsubscript{2}.\textsuperscript{27} The structural formula and transition temperature: of 10.O.NCS are given in Table 4.2.

X-ray studies

Experiments were carried out on aligned samples obtained by cooling slowly from the nematic phase. For probing the transition between smectic A phases, two types of X-ray investigations were carried out. For the Sm A\textsubscript{d}-Sm A\textsubscript{1} transition which involves large change in the layer spacing, d, a photographic setup was used. (These experiments were carried out at the Technical University of Berlin). In this case, the resolution in the determination of layer spacing d is ±0.2Å, the temperature accuracy being ± 25 mK. For studying the Sm A\textsubscript{d}-Sm A\textsubscript{2} transition where the change in d is small, the computer controlled guinier diffractometer described in Chapter 2 was used. In this case, precision in the determination of wave vector is 2×10^{-4}Å\textsuperscript{-1} while the resolution in the equatorial direction is 1×10^{-3}Å\textsuperscript{-1}. The temperature was maintained to an accuracy of ±5 mK.
Studies on Sm A-Sm A phase boundaries

10.0. NCS

\[
\text{C}_{10}\text{H}_{21}\text{O} - \text{COO} - \text{O} - \text{NCS}
\]

4-n-decyloxy -(4'-isothiocyanatophenyl) benzoate

<table>
<thead>
<tr>
<th>Isotropic</th>
<th>(\rightarrow)</th>
<th>Sm A</th>
</tr>
</thead>
<tbody>
<tr>
<td>96.0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Table 4.2:** Structural formula and transition temperature (in °C) of 10.0.NCS.
4.3.2 Results and Discussion

Mixing of 11OPCBob in 10.0.NCS leads to a rich variety of phases and phase transitions between them. The temperature-concentration (T-X, X is the mole fraction of 11OPCBob in the mixture) phase diagram of 10.0.NCS and 11OPCBob is shown in figure 4.38. The phases were identified by optical microscopy in conjunction with X-ray studies on aligned samples. For all mixtures, Sm $A_d$ phase is the higher-temperature smectic A phase, with Sm $A_1$ as the lower temperature phase for lower values of X and Sm $A_2$ for $0.8 < X < 1$. For intermediate X, the ribbon phase Sm $C$ is seen to intervene. For $0.48 < X < 0.67$ the Sm $A_d$ and Sm $A_1$ phases are separated by a re-entrant nematic phase.

X-ray experiments have been carried out on four different concentrations, namely $X=0.47, 0.69, 0.94 & 0.97$. Figures 4.39-4.42 shows the thermal variation of layer spacing for all these concentrations. The results show that

1. For $X=0.47$, a continuous evolution between Sm $A_d$ and Sm $A_1$ is seen (see figure 4.39).

2. First order Sm $A_d$-Sm $A_1$ transition marked by a jump in the layer spacing is seen for $X=0.69$ (see figure 4.40). The value of d drops from $50\text{Å}$ to $32\text{Å}$ at the transition.

3. Figure 4.41 shows a first order Sm $A_d$-Sm $A_2$ phase transition with a two phase coexistence region for $X=0.94$.

4. For $X=0.97$, Sm $A_d$ is seen to evolve continuously to Sm $A_2$ phase without a phase transition (see figure 4.42).
Studies on $Sm$ A-$Sm$ A phase boundaries

Figure 4.38: Temperature-concentration (T-X) phase diagram of 10.O.NCS-11OPCBOB system. X is the mole fraction of 11OPCBOB in the mixture. The continuous evolution leading from $Sm$ A$_1$ to $Sm$ A$_d$ surrounds the closed loop reentrant-nematic domain($N_{re}$), while the supercritical evolution between $Sm$ A$_d$ and $Sm$ A$_2$ is seen near the $Sm$ A$_d$-$Sm$ A$_2$ critical point C. Arrows indicate the concentrations of individual mixtures used for the X-ray experiments.
Figure 4.39: Temperature dependence of the smectic layer spacing $d$ for $X=0.47$ showing a supercritical evolution from Sm $A_d$ to Sm $A_1$ phase.
Figure 4.40: Thermal variation of $d$ for $X=0.69$ exhibits a first order Sm $A_d$-Sm $A_1$ transition.
Studies on Sm A-Sm A phase boundaries

Figure 4.41: Temperature variation of $d$ for $X=0.94$ shows a first order Sm $A_d$-Sm $A_2$ transition.
Studies on Sm A-Sm A phase boundaries

Figure 4.42: Temperature variation of $d$ for $X=0.97$ shows a continuous evolution from Sm $A_d$ to Sm $A_2$ phase.
Thus it is clear that the first order $\text{Sm } A_d - \text{Sm } A_2$ phase boundary is terminating at a critical point $C$, followed by a region of continuous evolution, with the critical point concentration lying between $X=0.94$ and $X=0.97$. Absence of $\text{Sm } C$ between $\text{Sm } A_d$ and $\text{Sm } A_2$ for $X>0.94$ has been confirmed by careful optical studies. These studies, carried out by slowly cooling a homeotropically aligned sample across the transition, did not show any birefringence, characteristic of the onset of $\text{Sm } C$ phase. A similar experiment, carried out on $X<0.90$ mixtures, clearly showed a narrow region of the $\text{Sm } C$ phase.

Thus the phase diagram given in figure 4.38 shows that there exists a continuous thermodynamic path between $\text{Sm } A_1$ and $\text{Sm } A_2$ phases. This path is seen to traverse via a $\text{Sm } A_d$ phase, i.e., $\text{Sm } A_1$ first evolves continuously into $\text{Sm } A_d$ and then into $\text{Sm } A_2$, thereby showing that the global symmetry of $\text{Sm } A_1$, $\text{Sm } A_d$ and $\text{Sm } A_2$ phases are the same.

Another interesting aspect of the phase diagram is that the $\text{Sm } A_d - \text{Sm } A_2$ part of the phase boundary terminates at a critical point, while the $\text{Sm } A_d - \text{Sm } A_1$ part of the boundary ends as a closed-loop nematic domain. Although the existence of $\text{Sm } A_d - \text{Sm } A_2$ critical point as well as a closed loop nematic domain at the terminus of $\text{Sm } A_d - \text{Sm } A_1$ has been predicted theoretically\textsuperscript{7-8,21} and observed experimentally\textsuperscript{9-10,19-20,22-24} the possibility of their existing together at the two ends of the phase boundary in a single phase diagram has not been considered before. Our experimental phase diagram shows the occurrence of such a situation.

It should also be noted that the occurrence of $\text{Sm } C$ phase in the phase diagram is in accordance with the theoretical phase diagram. It is expected that $\text{Sm } C$ is stable instead of $\text{Sm } A$ in the vicinity of partially bilayer $\text{Sm } A_d$\textsuperscript{28}.\textsuperscript{28}
Studies on Sm A-Sm A phase boundaries

References


[15] 11OPCBOB and 90BCB are kindly given to us by Prof. G.Heppke.


Studies on Sm A-Sm A phase boundaries


