CHAPTER 7

PHASE DIAGRAM

Phase diagram is constructed from the data of transition temperatures possessed by the individual complexes elucidated by DSC in the cooling run. Phase diagram of a homologous series gives information about the phase polymorphism, the thermal width of the individual phases and the variation of phase boundaries. Few interesting observations like the presence of odd-even effect on the phase variation, quenching of the phases and origination of the phases can be evinced. The phase abundance and the effect of alkyl/alkyloxy carbon number on the phases can also be studied.

7.1 INTRODUCTION

Seventeen homologous series are studied and their respective phase diagrams are discussed. Table 7.1 indicates the homologous series and their corresponding phase diagram figure number. The points drawn from the phase diagram are elaborately discussed for individual series. In the case of monotropic transition or second order transition of a particular complex, the transition temperature of that transition is borrowed from POM studies. All the transition temperatures are taken from the exothermic run of DSC.
### Table 7.1  Phase diagram of individual homologous series of HBLC and HBFLC

<table>
<thead>
<tr>
<th>S.No</th>
<th>Homologous series</th>
<th>Phase diagram number</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>HQ+nBAO</td>
<td>7.1</td>
</tr>
<tr>
<td>2</td>
<td>HQ+nBA</td>
<td>7.2</td>
</tr>
<tr>
<td>3</td>
<td>MHQ+nBAO</td>
<td>7.3</td>
</tr>
<tr>
<td>4</td>
<td>RI+nBAO</td>
<td>7.4</td>
</tr>
<tr>
<td>5</td>
<td>RI+nBA</td>
<td>7.5</td>
</tr>
<tr>
<td>6</td>
<td>ClBAO+nBAO</td>
<td>7.6</td>
</tr>
<tr>
<td>7</td>
<td>CBA+nBAO</td>
<td>7.7</td>
</tr>
<tr>
<td>8</td>
<td>IBAO+nBAO</td>
<td>7.8</td>
</tr>
<tr>
<td>9</td>
<td>MA+nBA</td>
<td>7.9</td>
</tr>
<tr>
<td>10</td>
<td>5BAO+mBAO</td>
<td>7.10</td>
</tr>
<tr>
<td>11</td>
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<td>16</td>
<td>11BAO+mBAO</td>
<td>7.16</td>
</tr>
<tr>
<td>17</td>
<td>12BAO+mBAO</td>
<td>7.17</td>
</tr>
</tbody>
</table>
Figure 7.1 Phase diagram of HQ+nBAO homologous series

Phase diagram of hydroquinone and alkyloxy benzoic acids is depicted in Figure 7.1. The following points can be elucidated from this Figure 7.1.

i) The HQ+nBAO hydrogen bonded homologous series exhibits orthogonal and tilted phases namely nematic and smectic C, smectic F, smectic G phases respectively.

ii) Total thermal range of the mesogenic phases increased with increase in the alkyloxy carbon number up to octyloxy carbon and then starts to decrease till dodecyloxy benzoic acid.

iii) Nematic phase is observed in all the complexes of the present homologous series.

iv) The smectic C phase is induced in the higher homologous members from heptyloxy benzoic acid and continued till
dodecyloxy carbon. The thermal phase width is largest for undecyloxy carbon and narrowest for dodecyloxy carbon.

v) A higher ordered phase smectic G phase is observed in HQ+10BAO complex quenching smectic F phase thermal range.

vi) A systematic decrease in the crystallization temperatures is observed up to octyloxy benzoic carbon number up on which the crystallization temperatures starts to increase proportionally along with its corresponding carbon number.

vii) One of the interesting observation in the present series is the detection of odd-even effect at isotropic to nematic phase transition with respect to enthalpy values and the corresponding transition temperatures.

7.3 PHASE DIAGRAM OF HQ+nBA HOMOLOGOUS SERIES

![Phase Diagram](image)

Figure 7.2 Phase diagram of HQ+nBA homologous series
Phase diagram of hydroquinone and alkyl benzoic acids is depicted in Figure 7.2. The following points can be elucidated from this Figure 7.2.

i) The HQ+nBA hydrogen bonded homologous series exhibits orthogonal and titled phases namely nematic and smectic F, smectic G phases respectively.

ii) Nematic phase is observed from carbon number 4 to 8 of the present homologous series.

iii) The smectic F phase is induced from carbon number 4 to 8. The thermal phase width is largest for undecyloxy carbon and narrowest for dodecyloxy carbon.

iv) A higher ordered phase smectic G phase is observed only in HQ+2BA complex.

7.4 PHASE DIAGRAM OF MHQ+nBAO HOMOLOGOUS SERIES

Figure 7.3 Phase diagram of MHQ+nBAO homologous series
Phase diagram of methoxy hydroquinone and alkyloxy benzoic acids is depicted in Figure 7.3. The following points can be elucidated from the Figure 7.3.

i) MHQ+nBAO hydrogen bonded homologous series exhibit orthogonal phase nematic and tilted phases smectic C, smectic F and smectic G phases respectively.

ii) Nematic phase is observed in all the complexes of the present homologous series with varying thermal width.

iii) Smectic C phase is appeared in the higher homologous members from heptyloxy benzoic acid and continued till dodecyloxy carbon. As the chain length increase, the corresponding l/d ratio of the mesogen is responsible for the induction of smectic C phase.

iv) A higher ordered phase, smectic F phase is observed in MHQ+11BAO and MHQ+12BAO complexes quenching the thermal range of smectic G phase.

7.5 PHASE DIAGRAM OF Rl+nBAO HOMOLOGOUS SERIES

![Phase diagram of Rl+nBAO homologous series](image)

Figure 7.4 Phase diagram of Rl+nBAO homologous series
Phase diagram of resorcinol and alkyloxy benzoic acids is depicted in Figure 7.4. The following points can be elucidated from this Figure 7.4.

i) The R\textsubscript{l+n}BAO hydrogen bonded homologous series exhibits orthogonal and tilted phases namely nematic, smectic C and smectic F phases respectively.

ii) Nematic phase is observed in almost all the complexes of the present homologous series excepting in the complex of carbon number 5.

iii) The smectic C phase is induced from heptyloxy benzoic acid and continued till dodecyloxy carbon.

iv) One of the interesting observations in the present series is the detection of odd-even effect with respect transition temperatures at isotropic to nematic phase transition.

7.6 PHASE DIAGRAM OF R\textsubscript{l+n}BA HOMOLOGOUS SERIES

![Phase diagram of R\textsubscript{l+n}BA homologous series](image)

Figure 7.5 Phase diagram of R\textsubscript{l+n}BA homologous series
Phase diagram of resorcinol and alkyl benzoic acids is depicted in Figure 7.5. The following points can be elucidated from this Figure 7.5.

i) The Rl+nBA hydrogen bonded homologous series exhibits only smectic G phases.

ii) Smectic G phase is observed in all the complexes of the present homologous series.

iii) The thermal phase span of smectic G is almost unaltered throughout the series.

7.7 PHASE DIAGRAM OF CIBAO+nBAO HOMOLOGOUS SERIES

![Figure 7.6 Phase diagram of CIBAO+nBAO homologous series](image)

The phase diagram of the present CIBAO+nBAO homologous series is constructed from the DSC and POM data and is depicted in Figure 7.6 which reveals the following points:
i) Phase diagram is composed of three phases viz., nematic, smectic R and smectic C.

ii) Nematic phase prevails throughout the entire homologous series with a wide thermal range enabling the mesogens to be exploited for commercial applications.

iii) A new phase namely smectic R is induced at octyloxy and continued till the undecyloxy benzoic acid carbon number quenching the thermal span of nematic phase.

iv) The thermal range of smectic R is appreciable in all the compounds except heptyl alkyloxy carbon number varying from 6 °C to 25 °C.

v) Higher ordered phase namely smectic C is induced only in the undecyloxy carbon number quenching smectic R. The thermal span of smectic C is observed to be very narrow (~1.4 °C). The increase in the length of the mesogen altered the l/d ratio favoring the inducement of smectic C phase.

7.8 PHASE DIAGRAM OF CBA+nBAO HOMOLOGOUS SERIES

Figure 7.7 Phase diagram of CBA+nBAO homologous series
The phase diagram of CBA+nBAO series is depicted in Figure 7.7 which reveals the following points:

i) Phase diagram is composed of orthogonal and tilted phases viz., nematic, smectic C and smectic G.

ii) Nematic phase is observed in all the members of the present homologous series.

iii) Odd-even effect is observed in transition temperatures of isotropic to nematic transition.

iv) A note worthy point is that at even carbon numbers tilted phases are induced viz. at hexyloxy carbon number smectic G is induced while at octyloxy carbon number smectic C phase is induced.

v) The thermal span of the nematic is found to be greatly reduced with the induction of the higher ordered smectic C phase.

vi) The lower homologous have the larger thermal span of the nematic phase compared to their higher counter parts.

vii) The total mesogenic range in the present homologous series started to increase up to octyloxy carbon number and then it saturated with the further increment of the carbon number.
Phase diagram constructed with the results of transition temperatures and thermal stability exhibited by the IBAO+nBAO is presented in Figure 7.8. The salient features of the phase diagram for the IBAO+nBAO reflects up on:

i) The HBLCs viz., IBAO+nBAO exhibit nematic phase with orientational order, smectic D LC phase with homeotropic orthogonal alignment, tilted smectic phases with layering order, smectic R, smectic X, and smectic F respectively. Nematic phase prevails in all complexes which exhibited LC nature with varying thermal spans.

ii) LC phases are quenched in even numbered intermediate homologues (n = 8 and 10). Quenching is attributed to the effective transverse dipole moment $\mu_t$ inherently possessed by the molecule as I-atom is substituted at meta position of the 3-iodobenzoic acid.
iii) Two new phases, viz., smectic R and smectic X exhibiting hither to un-reported textures along with a rarely reported smectic D phase are exhibited by IBAO+nBAO, which is assumed due to the strategic position occupied to the electronegative I-atom with respect to the rigid core part of the LC complex.

iv) A quasi-2D ordered tilted hexagonally ordered smectic F phase is found to follow and occur by cooling the tilted 1-D tilted smectic C phase in the IBAO+nBAO prevalently in odd-numbered higher homologues.

v) Odd-even effect is found to occur at the crystal melting points (where crystal or solid phase changes in to LC phase with heating) as a consequence of alternating contributions of axial polarizabilities.

7.10 PHASE DIAGRAM OF MA+nBA HOMOLOGOUS SERIES

Figure 7.9 Phase diagram of MA+nBA homologous series
Phase diagram of the present homologous series is constructed with POM and DSC data and is illustrated as Figure 7.9. Following points can be drawn from the phase diagram.

i) Phase diagram is comprised of three chiral phases viz. cholesteric, smectic X*, and smectic G*.

ii) An interesting observation is that all the mesogens of this series are mono-phase variant. An exception to this is MA+8BA which is a bi-phase variant. Yet another feature is the appearance of higher ordered smectic G* phase in the first (MA+2BA) and in the last (MA+8BA) homologues of the series.

iii) The thermal mesogenic range gradually increased with the increment in the alkyl carbon number. It is maximum for MA+5BA (26.1°C) and minimum for MA+2BA (2°C).

iv) New phases have been induced at regular intervals of the alkyl carbon number. In MA+5BA smectic G* phase is completely quenched by smectic X* while smectic X* has been completely quenched in MA+7BA paving way for cholesteric phase. In MA+8BA, quenching the cholesteric phase, smectic G* reappeared.

v) No odd-even effect is observed in the phase transition temperatures. However, isotropic to liquid crystalline phase transition temperature and the liquid crystalline phase to crystal phase transition temperatures are almost unaltered for five complexes viz., MA+4BA to MA+8BA.
vi) Smectic G* is induced in the lower order homologous series with an exception of MA+8BA, which may be attributed to the decrease in chain length which makes the molecules more stable exhibiting higher order phases.

vii) A new phase labeled as smectic X* is observed in the pentyl and hexyl carbon number homologous series. Further, this phase is sandwiched by isotropic and crystal. Complexes possessing smectic X* phase melt at low temperatures when compared to the other complexes. This clearly shows that presence of smectic X* phase has drastically reduced the melting temperature. A wide thermal range of smectic X* is noticed in both the complexes viz., MA+5BA and MA+6BA.

7.11 PHASE DIAGRAM OF 5BAO+mBAO HOMOLOGOUS SERIES

![Phase diagram of 5BAO+mBAO homologous series](image)

Figure 7.10 Phase diagram of 5BAO+mBAO homologous series
Figure 7.10 illustrates the phase diagram of 5BAO+mBAO homologous series. Following points can be elucidated from the phase diagram.

i) The phase diagram is composed of five phases viz. nematic, smectic X, smectic C, smectic G and smectic F.

ii) Nematic phase is observed in all the complexes of this series.

iii) A new phase namely smectic X with noticeable thermal range (~1.0 °C) is observed in 5BAO+11BAO complex.

iv) The tilted smectic C phase has quenched the nematic in the higher carbon number namely octyl and prevails throughout the series. It can be reasoned out the increased chain length altered the l/d ratio and thus it favored the occurrence of smectic C phase.

v) Smectic C has a wide thermal span which can be clearly identified from the Figure 7.10.

7.12 PHASE DIAGRAM OF 6BAO+mBAO HOMOLOGOUS SERIES

Figure 7.11 Phase diagram of 6BAO+mBAO homologous series
Figure 7.11 illustrates the phase diagram of 6BAO+mBAO homologous series. Following conclusions can be made from the phase diagram.

i) The phase diagram is comprised of five phases viz. nematic, smectic X, smectic C, smectic F and smectic G.

ii) Nematic phase is observed in all the members of the series.

iii) The thermal width of tilted smectic C phase is comparatively larger in 6BAO+9BAO while in the higher homologous members (6BAO+10BAO, 6BAO+11BAO and 6BAO+12BAO) the thermal phase width continues to increase with increase in the carbon number.

iv) Smectic X phase with considerable thermal range (~1.5°C) is observed in 6BAO+10BAO complex.

v) Crystallization temperatures corresponding to the lower homologues are elevated in the present series with respect to the earlier 5BAO+mBAO series.

7.13 PHASE DIAGRAM OF 7BAO+mBAO HOMOLOGOUS SERIES

![Phase diagram of 7BAO+mBAO homologous series](image)

Figure 7.12 Phase diagram of 7BAO+mBAO homologous series
Figure 7.12 shows the phase diagram of 7BAO+mBAO homologous series. Following points can be derived from the phase diagram.

i) The phase diagram of this present series consists of four phases namely nematic, smectic X, smectic C, and smectic F.

ii) Here in this phase diagram also the l/d ratio is the dominating reason for the observation of smectic C phase from the octyl series and to be continued for the entire series.

iii) Smectic X is observed in 7BAO+10BAO complex with 2.2°C thermal width.

iv) The quenching of smectic C with smectic F is observed. Increase in the chain length has thus favored a more ordered phase (smectic F).

v) It is interesting to note the odd-even effect at the smectic C to smectic F phase transition temperatures.

7.14 PHASE DIAGRAM OF 8BAO+mBAO HOMOLOGOUS SERIES

Figure 7.13 Phase diagram of 8BAO+mBAO homologous series
Phase diagram of the present homologous series is constructed with POM and DSC data and is illustrated in Figure 7.13. Following points can be drawn from the phase diagram.

i) The phase diagram is comprised of four phases viz. nematic, smectic X, smectic C, and smectic F.

ii) All the complexes possess a wide thermal span of the mesogenic phases.

iii) Smectic X phase with a narrow thermal range (~0.5°C) is observed only in 8BAO+12BAO complex.

iv) Higher ordered smectic phase F is observed in two complexes possessing carbon number nonyl and decyl respectively.

v) The higher ordered smectic F phase is quenched by the smectic C phase as the carbon number increases beyond.

7.15 PHASE DIAGRAM OF 9BAO+mBAO HOMOLOGOUS SERIES

Figure 7.14 Phase diagram of 9BAO+mBAO homologous series
Figure 7.14 illustrates the phase diagram of 9BAO+mBAO homologous series. Following points can be concluded on observing the diagram.

i) The phase diagram is comprised of four phases viz. nematic, smectic X, smectic C, and smectic F.

ii) Orthogonal phase nematic and tilted phase smectic C are observed in all the homologues.

iii) Odd-even effect is not observed at isotropic to nematic interface either in transition temperatures or in enthalpy values.

iv) Narrow thermal range of nematic phase observed in all the complexes is unaltered with chain length.

v) Smectic X phase sandwiched between nematic and smectic C has a reasonable thermal range (~3.3°C) in 9BAO+ 12BAO complex.

vi) The total mesogenic thermal range is almost unaltered with the chain length.

7.16 PHASE DIAGRAM OF 10BAO+mBAO HOMOLOGOUS SERIES

Figure 7.15 Phase diagram of 10BAO+mBAO homologous series
Phase diagram of p-n-decyloxy benzoic acid and p-n-alkyloxy benzoic acids (10BAO+mBAO) homologues series is depicted in Figure 7.15. The following points can be elucidated from Figure 7.15:

i) Phase diagram is composed of four phases viz. nematic, smectic X, smectic C, and smectic F.

ii) Lower homologues have a wider thermal span of nematic phase while the higher homologues has comparatively narrow thermal span.

iii) A new smectic ordering labeled as smectic X, with a varying thermal range is observed in three complexes viz., 10BAO+6BAO, 10BAO+7BAO and 10BAO+12BAO.

iv) It is noteworthy to mention that the Smectic C phase is observed in all the complexes of the series.

7.17 PHASE DIAGRAM OF 11BAO+mBAO HOMOLOGOUS SERIES

Figure 7.16 Phase diagram of 11BAO+mBAO homologous series
Phase diagram of p-n-undecyloxy benzoic acid and p-n-alkyloxy benzoic acids (11BAO+mBAO) homologues series is depicted in Figure 7.16. The following points can be elucidated from Figure 7.16:

i) The phase diagram consists of four phases viz. nematic, smectic X, smectic C, and smectic F.

ii) It is interesting to note that smectic X phase is observed in the first (11BAO+5BAO) and last members (11BAO+12BAO) of the homologous series with a narrow thermal span.

iii) Nematic and smectic C phases are observed in all the alkyloxy carbon numbers. Quenching of the nematic phase by smectic C is observed as the carbon chain length increases.

iv) A wide range of thermal span of smectic C is observed in the series.

v) A new smectic ordering labeled as smectic X is observed and characterized. In an identical homologous series a similar phase has been characterized using different techniques.

vi) It is surprising to note that smectic F, the highly oriented phase is observed only in the 11BAO+9BAO complex.

vii) The over all mesogenic thermal range possessed by individual complexes of the series has decreased with the increment in carbon number.

viii) Odd even effect is not observed at isotropic to nematic interface either in transition temperatures or in corresponding enthalpy values.
7.18 PHASE DIAGRAM OF 12BAO+mBAO HOMOLOGOUS SERIES

Figure 7.17 illustrates the phase diagram of 12BAO+mBAO homologous series. Following conclusions can be made from the phase diagram.

i) Phase diagram consists of four phases viz. nematic, smectic X, smectic C, and smectic F.

ii) Thermal phase width of nematic is larger in lower homologous compounds compared to the higher counter parts.

iii) Four compounds (12BAO+8BAO, 12BAO+9BAO, 12BAO+10BAO and 12BAO+11BAO) exhibiting smectic X phase with varying thermal ranges.

iv) Smectic F, the highly ordered phase is observed only in the 12BAO+7BAO complex with large thermal span.
7.19  CONCLUSION

Phase diagrams of all the seventeen homologous series are constructed based upon the DSC data.

The phase sequence obtained in the homologous series, inducement of new phases, quenching of a particular phase with respect to the alkyl carbon number are elaborated in this chapter.

Phase diagram gives valuable information about mesogenic properties of homologues such as phase abundant, their thermal range, transition temperature, inducement and quenching of mesophase with respect to the change in the carbon number.