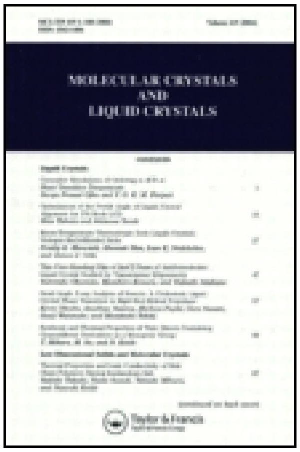

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Weak Forces for the Growth of Smectic-F Liquid Crystal

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Weak Forces for the Growth of Smectic-F Liquid Crystal

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N(*p*-*n*-dodecyloxybenzylidene)*p*-*n*-alkylanilines, viz., 12*O*.*m* compounds of *nO*.*m* series, for $m = 4$, 5, 6, 8, 10, 12, 14 and 16 are synthesised and characterised by Polarised Thermal Microscopy (TM) and Differential Scanning Calorimetry (DSC). These compounds are found to exhibit 2D Bond-Orientationally (BO) ordered smectic-F liquid crystal phase with shift distortion along with orthogonal smectic-A, -B(cryst) phases. The intermediate members of the compounds of 12*O*.*m* series ($m < 10$) are found to exhibit orthogonal smectic phases along with the tilted phases, while the higher homologues ($m > 10$) show the tilted bond-orientational smectic phases only. The miscibility studies for the confirmation of smectic-F phase through binary (12*O*.12 + 10*O*.14) phase diagram, suggests the possibility for the occurrence of smectic-F phase down towards ambient temperatures. The smectic-G phase melting temperature, T_{FG} is found to depress at lower and higher concentrations (x), while smectic-F phase clearing temperature T_{IF} remains constant with the concentration. The thermal span of smectic-F phase is found to depend on the chemical potential (represented by the mole fraction x) in the (T, x) phase diagram. The cubic fit in the vicinity of lower/higher concentrations, qualitatively infers the weak nature of Van der Walls' molecular forces for the growth of pseudo-hexagonal packed quasi-2-D BO ordered S_F liquid crystal with a poor registry of positional correlations.

Keywords: 12*O*.*m* compounds of *nO*.*m* series; smectic-F; miscibility studies; phase diagram; Van der Walls' forces

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INTRODUCTION

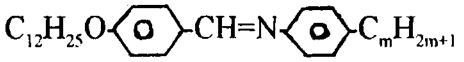
Ever since the discovery of first liquid crystal (LC), the research on these materials has been witnessing a steady growth regarding the discovery and identification of a number of nematic and smectic phases characterised by their lower dimensional crystalline order. However, in the recent times, the tilted smectic phases with tilt and bond orientational (BO) structural order heralded a new era of LC experimental research owing to their ability to cater the much needed experimental proof for the theoretically predicted [1, 2] Thouless-Kosterlitz 2-D crystal melting and the Harmonic Scaling theory. The higher order non-linear optical properties exhibited by the relatively condensed tilted chiral smectic phases (with fast sub-micro second time response than the sluggish milli-second classical nematic liquid crystal) evoked much response for the design of molecules which exhibit the condensed chiral phases down to ambient temperatures for their use in electro-optical displays. Further, the fundamental aspects of research to infer the nature of molecular forces responsible for the growth, thermal stability and increase of its thermal span is felt to reveal an inkling for the realisation of these relatively condensed BO smectic-F and -I phases and their chiral analogues down to the ambient temperatures for their applicational viability.

The meagre smectic-F experimental data for a possible occurrence in the relatively higher homologues [3] in a LC series and the recently observed [4 – 8] piezoelectric response, suggest for a systematic experimental study for its' occurrence and thermal abundance in the domain of varying molecular chemistry. The body of the data available on various schiff base thermotropic LC systems (such as mono component and binaries) show [9 – 13] the occurrence of a variety of smectic phases involving BO order and serve the required experimental opportunity for the proposed systematic studies to infer the influence of chemical potential for the optimal thermal stability conditions of smectic-F phase.

The present work involves the synthesis and characterisation of smectic-F phase in the 12*O.m* compounds (of *nO.m* homologous series) and its confirmation through binary phase diagram using polarised thermal microscopy and differential scanning calorimetry techniques. An attempt is made to understand the nature of inter-molecular forces and the effect of inter molecular potential for the growth of shift distortion mediated smectic-F phase with the pseudo-hexagonal ordering.

EXPERIMENTAL

The compounds of 12*O*.*m* (for $m = 4$ to 16) series of LC schiff base *nO*.*m* compounds viz., N(*p*-*n*-alkoxybenzylidene)*p*-*n*-alkylanilines were synthesised from the *p*-dodecyloxybenzaldehyde and the respective *p*-*n*-alkylanilines by the condensation reaction as reported [9] earlier. A Hertel-Reuss (super pan II) polarising microscope was used for the textural studies in conjuction with a PC monitored INSTEC mK temperature controller to an accuracy of ± 0.01 K. The required binary LC systems were prepared by mixing the 12*O*.12 with 10*O*.14 at different weight fractions with the help of an Electrical balance (±0.1mg) of Dhona 200D for the confirmation of smectic-F. Perkin Elmer DSC-7 system was used to record the transition temperatures and the enthalpies involved at the transitions. The molecular formula for the 12*O*.*m* compounds is



RESULTS AND DISCUSSION

The phase transition temperatures, T_C observed through polarised thermal microscopy (with their characteristic textures [14]) and Differential Scanning Calorimetry (at 5°C per minute) along with the transition enthalpy ΔH values are given in Table I. It is observed that the thermal span of the respective LC phases in 12*O*.4 is found to agree with the reported [15] values, where the unidentified smectic phases are confirmed as smectic-B and G by following miscibility studies. It may be noticed that the smectic-B_{cryst}, (structurally different from smectic-$B_{hexatic}$), occurring in 12*O*.*m* series is characterised [14] by the observation of transient transition bars across the focal conic fans (generally observed in *nO*.*m* compounds) while it grows from the smectic-A phase. However, the smectic-F phase in these compounds is confirmed by using the rule [16] of selective miscibility. It is also observed that there is a slight disagreement between crystallisation temperatures from TM and DSC due to the different rates of cooling and other conditions employed, which is often encountered. However, the considerable difference in the crystal cooling temperature and the melting temperature in the case of 12*O*.14 may be a case of a premature supercooling.

TABLE I The transition temperatures in °C and enthalpy values in J/gm for different transitions in 12*O.m* compounds

12*O.m* Compounds		*Transition temperatures in °C and Enthalpy, ΔH in J/gm*						
m	*Method*	*Iso-A*	*Iso-F*	*A-B*	*A-F*	*B-G*	*F-G*	*G-Cryst.*
4	TM	82.50		72.50		69.00		55.00
	DSC-Cooling	82.95(18.97)		72.44(10.78)		69.60(0.16)		–
	-Heating	85.61(19.12)		75.32(11.11)		72.60(0.17)		55.11(69.63)
5	TM	88.00		81.00		61.50		50.00
	DSC-Cooling	88.76(20.13)		80.09(11.40)		–		–
	-Heating	91.59(20.79)		82.35(11.89)		–		51.83(66.23)
6	TM	87.50		80.00		77.00		50.00
	DSC-Cooling	87.01(19.30)		80.95(13.49)		–		–
	-Heating	89.78(20.01)		83.45(13.74)		–		49.22(57.14)
8	TM	89.00			87.50		85.00	53.00
	DSC-Cooling	89.17(16.67)			86.25(10.95)		–	–
	-Heating	91.10(15.89)			88.33(10.74)		–	54.25(81.45)
10	TM	89.50			89.00		87.00	60.00
	DSC-Cooling	90.46(9.65)			89.53(13.14)		–	–
	-Heating	91.55(–)			90.80(–)		–	61.97(110.05)
12	TM		88.00				86.50	68.00
	DSC-Cooling		87.70(33.35)				–	–
	-Heating		90.32(32.43)				–	68.54(103.27)
14	TM		87.40				86.40	73.00
	DSC-Cooling		87.40(34.14)				86.40	45.60(84.78)
	-Heating		89.90(35.03)				88.90	74.00(124.30)
16	TM		88.1				86.90	78.10
	DSC-Cooling		85.25(36.80)				–	45.03(84.78)
	-Heating		88.1(34.53)				86.98	78.06(127.96)

Values given in the paranthesis represent the enthalpy values in J/gm.

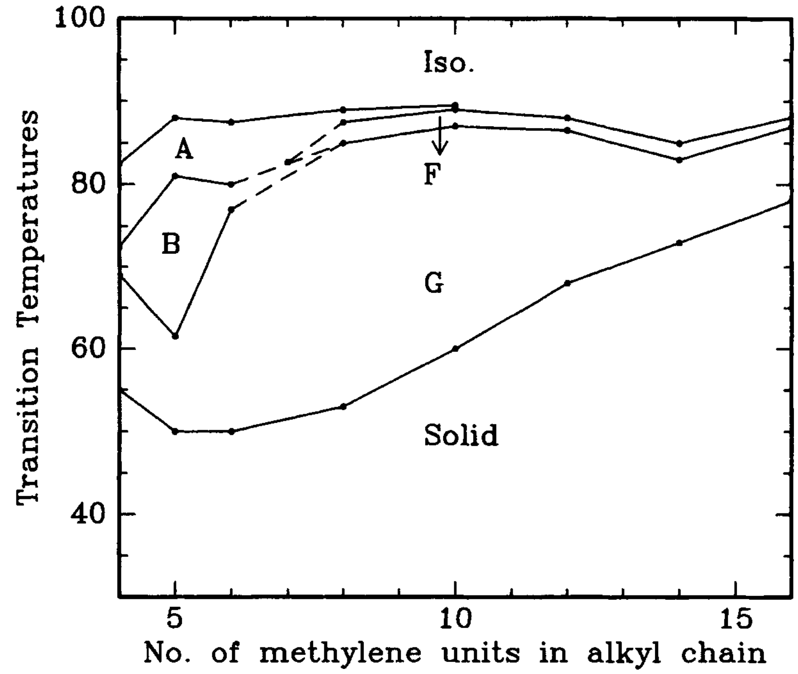


FIGURE 1 Phase diagram of 12*O*.*m* compounds.

The phase diagram along with the phase sequences exhibited by different compounds of 12*O*.*m* (for $m = 4, 5, 6, 8, 10, 12, 14$ and 16) series is given in Figure 1. The Figure 1 reveals that

1. The compounds with $m < 10$ prevalently exhibit orthogonal smectic-A and smectic-B(cryst) phases along with the smectic-G phase which appears in all the compounds with varying thermal range,
2. The increase of alkyl end chain length enhances the occurrence of hexagonal tilted phases like smectic-F and smectic-G,
3. A direct smectic-F phase results from the isotropic liquid phase for alkyl chain length m with the quenching of both orthogonal phases viz., smectic-B ($m > 7$) and smectic-A phase ($m > 10$),
4. The thermal stability (as observed through constant T_{IF}) is almost constant for the smecitc-F phase, even though the temperature of its occurrence varies with m value, and
5. The smectic-G attains maximum stability for the intermediate compounds, while its stability is relatively less in lower as well as in higher homologues.

The occurrence of tilted 2-D liquid crystal phase (directly from the isotropic liquid) in the higher homologues of 12*O*.*m* series with the increasing alkyl end chain is found in agreement with our previous systematic studies of TBnA [10, 11] and 10*O*.*m* [13] series of LC compounds. However, the confirmation of smectic-F phase in 12*O*.12 (as a representative case since m = 14 and 16 exhibit similar textures) is carried out through the systematic miscibility (binary) studies with the 10*O*.14 compound exhibiting [13] FG variant. The miscibility phase diagram of (12*O*.12 + 10*O*.14) is presented in Figure 2. The preliminary identification of smectic-F phase grown from the cooled isotropic liquid of 12*O*.12, 14 and 16 and its confirmation is carried out by taking a small speck of the sample on the microscopic glass slide, which exhibited a six sectored (Plate-1 for 12*O*.12) polygon under the crossed polars characteristic of smectic-F liquid crystal in agreement with the reported [14] texture. From the miscibility studies (Fig. 2), it is inferred that

1. The FG variant exhibited by the compound 12*O*.12 is found continuously miscible at all compositions of 12*O*.12 in 10*O*.14, confirming the phase variant of 12*O*.12 as FG (12*O*.14 and 16 also exhibit similar results),
2. The liquid crystalline clearing (T_{IF}) temperatures are found to remain almost constant as both the compounds 12*O*.12 and 10*O*.4 bear the same molecular weight,

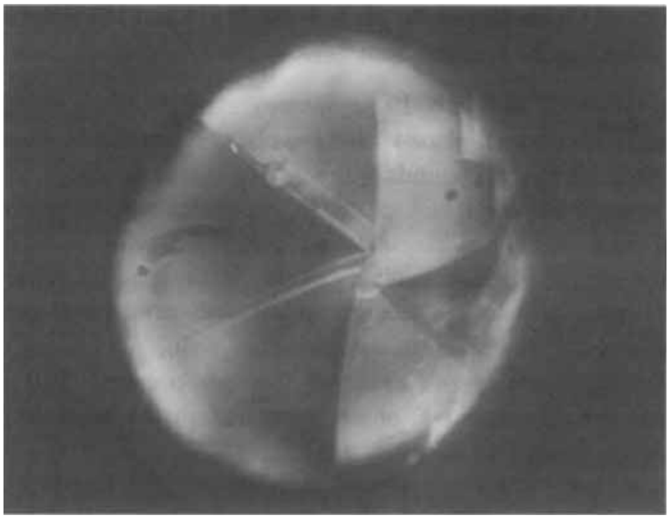


PLATE 1 (See Color Plate I).

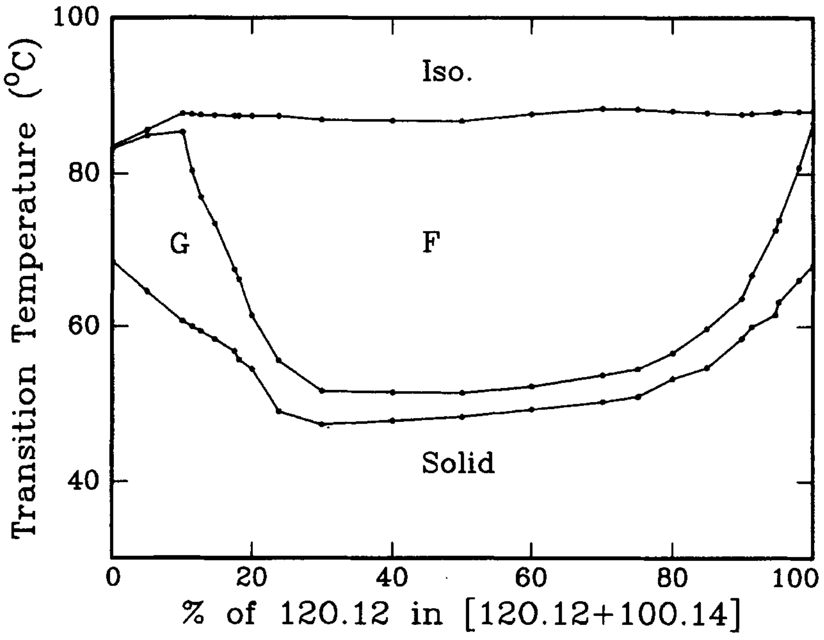


FIGURE 2 Miscibility diagram of binary 12*O*.12 + 10*O*.14.

3. The smectic-F phase possesses lower thermal span at either ends of the compositions of the binary phase diagram. However, it is found to possess larger span in between 30% and 90% concentrations to suggest the midway optimum chemical potential for the smectic-F abundance. Further, a careful observation of the binary phase diagram suggests that smectic-F thermal span ($\Delta T_F = T_{IF} - T_{FG}$) is increased by increasing the % of composition of 12*O*.12 in 10*O*.14 (0–30%) or by increasing the 10*O*.14 in 12*O*.12 (100–60%) as observed through the decreasing smectic-F to smectic-G transition temperature T_{FG}, inspite of the constant smectic-F clearing point, T_{IF}. This feature of the binary phase diagram provides an opportunity for the selection of a proper composition of the binary to realise the smectic-F phase down to the ambient temperatures for its operational viability,
4. The smectic-G phase is found to possess the least and almost constant thermal span ($T_{FG} - T_{cryst.}$) at the intermediate compositions of the phase diagram (where smectic-F exhibited maximum span). However, the increasing G-thermal stability at the end compositions reflect the fact that the long range positional order of smectic-G phase is easier to establish in a single component system than in the mixtures and

5. The smectic-G to crystal (solid K) boundary is almost similar to that of the phase diagram of 12*O.m* (Fig. 1) compounds to infer the similarity of the relevant chemical potential for G-solid (K) interface.

These results (3 and 4 points), motivated us to further investigate the interesting and exotic behaviour of the binary composition with smectic-F thermal span, i.e., smectic-F tuned through the chemical potential to infer the nature of intermolecular forces responsible for the formation of pseudo-hexagonally packed long range bond-orientational order. It may be argued that the observed composition dependence on $[\Delta T]_F = [T_{IF} - T_{FG}]$ may not reflect the growth of long range bond orientational due to the fact that whether S_G or S_F, both possess long range bond orientational order (not withstanding the observations that T_{IF} remains constant, while T_{FG} effectively depresses with x). However, a careful structural overview of the Smectic-G/Smectic-F boundary reveals [14] the difference between bond orientational order involved with them. The smectic-G is a true 3-D BO phase with additional positional correlations within the layers, while smectic-F is 2D phase with BO order characteristic of shift distortions and is responsible for the pseudo-hexagonal packing with poor registry of positional correlations. Smectic-F BO order is distinguished with short range order of molecular positions within layers. Further, the hexagons of smectic-F liquid crystal of one layer could skid to the next layer. It may be seen that the enhancement of the smectic-F liquid crystal's thermal span is effectively controlled by the composition in the binary at the either ends only, while the changing composition ceases to show its effect at the mid portion of the (T, x) diagram. From the Figure 2, it is noticed that FG transition temperature undergoes depression with x (representing the chemical potential) on either sides of the diagram. However, T_{FG} remains almost constant in the mid portion of it. Thus, the smectic-G phase distinct (a 3D BO ordered phase) with long range positional correlations appears to be squeezed with increasing x. In order to study the influence of chemical composition x for the growth of smectic-F liquid crystal thermal span, a meticulous analysis of x as a variable for F-span is needed effectively in the two regions (where T_{FG} undergoes depression around 0–30% and an elevation around 60–100% of x).

The thermal range of smectic-F i.e. $(T_{IF} - T_{FG})$ plotted against the concentration (x) of 12*O*.12 in 10*O*.14 (reflecting the chemical potential as a representative (T, x) diagram) is shown in Figure 3. The present case of the equivalent (T, x) diagram is aimed to study the effect of composition/chemical potential (x) on the growth of smectic-F liquid crystal thermal

TABLE II The transition temperatures, smectic-F range and normalized smectic-F ranges of various compositions of 12*O*.12 in the binary 12*O*.12 + 10*O*.14

% of 12*O*.12 *in the binary*	*I-F Temp.* T_{IF} (°*C*)	*F-G Temp.* T_{FG} (°*C*)	*G-Solid Temp.* T_{GK} (°*C*)	*F Range* ΔF = $[T_{IF} - T_{FG}]$	$\Delta F/\Delta F_{max}$
0.00	83.50	83.20	68.50	0.30	0.0085
5.00	85.64	84.90	64.58	0.74	0.0210
10.00	87.74	85.36	60.68	2.38	0.0674
11.30	87.62	80.37	59.98	7.35	0.2081
12.51	87.56	76.93	59.35	10.63	0.3011
14.50	87.48	73.42	58.32	14.06	0.3982
17.40	87.43	67.43	56.81	20.00	0.5664
18.06	87.43	66.18	55.68	21.25	0.6020
20.00	87.43	61.42	54.50	26.01	0.7366
23.87	87.41	55.56	49.06	31.85	0.9021
30.00	86.93	51.67	47.38	35.26	0.9985
40.00	86.82	51.53	47.86	35.29	0.9986
50.00	86.72	51.41	48.37	35.31(max)	1.0000
60.00	87.62	52.31	49.33	35.31(max)	1.0000
70.00	88.31	53.70	50.27	34.61	0.9801
75.00	88.22	54.49	50.94	33.73	0.9552
80.00	88.02	56.58	53.29	31.44	0.8903
85.00	87.80	59.71	54.67	28.10	0.7958
90.00	87.59	63.67	58.42	23.92	0.6774
91.37	87.71	66.70	59.96	21.01	0.5950
93.50	87.82	72.53	61.54	15.29	0.4330
95.17	87.90	73.88	63.22	14.02	0.3971
98.02	87.96	80.79	66.08	7.17	0.2031
100.00	88.00	86.50	68.00	1.50	0.0424

span. The effect of chemical potential in the binary system on the observed smectic-F thermal span (through smectic-G melting temperature T_{FG} and smectic-F clearing temperature T_{IF}) at different concentrations (0–30% through dotted line and 60–100% through a dotted line with the relevant parameters) is fitted to a cubic function of type given by

$$f(x) = a + bx + cx^2 + dx^3 \tag{1}$$

The variance values (along with constants a, b, c and d) specified in Figure 3 demonstrate the consistency of the fit. This cubic dependence of the chemical potential in the (T, x) diagram in the regions of compositions 0–30% and 60–100% is found comparable to the classical Van der Waals cubic equation for gases where the intermolecular forces are characterised to be weak natured. Further, it may be recalled that inert gas crystals are found [17] to possess weak intermolecualr forces of Van der Walls type. The role of chemical potential in the present S_F liquid crystal phase is to reflect the volume it sweeps under the influence of governing intermolecular force.

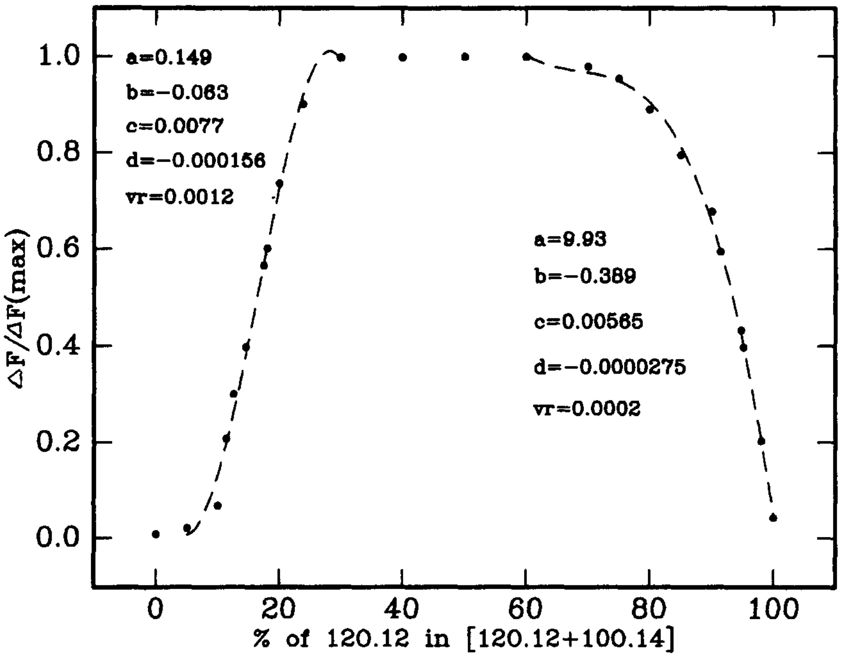


FIGURE 3 Normalised smectic-F range versus % of 12*O*.12 in 12*O*.12 + 10*O*.14. The variance along with the fit and the parameters are given for compositions 0–30%, (dotted line) and 60–100% (dotted line).

Thus, the growth of thermal span of S_F liquid crystal phase characteristic of long range BO order, pseudo-hexagonal packing and shift distortion is inferred as mediated through weak Van der Walls' type of intermolecular forces.

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