Dilatometric Study of the Isotropic-Smectic F Transition of 10O.14

N. V. S. Rao, G. Padmaja Rani, D. M. Potukuchi, and V. G. K. M. Pisipati

Centre for Liquid Crystal Research and Education, Faculty of Physical Sciences,
Nagarjuna University, Nagarjuna Nagar-522 510, India

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The compound N(p-n-decyloxy benzylidene)p-n-tetradecyl aniline, (10O.14), a higher homologue of the MBBA series, exhibits smectic F and smectic G phases. Dilatometric studies inferred strong pre-transitional effects in a large temperature range. DSC results confirmed the first order nature of the IF and FG transitions. The exponential growth of continuous six fold hexagonal order across the isotropic-smectic F phase transition is estimated from the density studies with an exponent $b = 0.75$.

Introduction

Investigations [1, 2] of smectic liquid crystals characterised by two and three-dimensional ordering (crystalline as well as hexatic) have motivated the study of phase transitions mediated by dislocation melting phenomena. The role of thermal fluctuations is yet to be explained by the harmonic scaling theory to account for the experimentally observed deviations. The growth of two-dimensional structural order and bond orientational order in the formation of the smectic F phase from the isotropic liquid is accompanied by a long range tilt ordering of molecules with long range ordering of hexagonal positional correlations. This arrangement leads to the possibility of sliding of the hexagons from one layer to the other. Even though the growth of such a six-fold hexatic ordering either from an isotropic liquid or a mesomorphic state requires a continuous growth of symmetry across the phase transition boundary, the long range two fold tilt order parameter interferes with the six fold hexatic symmetry. Hence, the coupling between positional and tilt orders becomes stronger, thereby making the analysis of the critical properties of the transition complex.

The liquid crystalline compounds exhibiting a smectic F phase, studied so far with high resolution [2] are no good examples of two dimensional melting since they all exhibit a mesophase above the smectic F phase, i.e. smectic F to liquid crystal mesophase phase transitions, which precludes the melting of a 2 D crystal into an isotropic fluid phase. However, synthesis of three benzoate esters [3] and one nO.m compound [4] exhibiting an isotropic to smectic F transition is reported. Hence one such compound, viz. 10O.14, exhibiting isotropic, smectic F and smectic G phases has been chosen for our phase transition studies.

The smectic F to smectic G transition involves the transition of tilted hexagonal smectic F with 2-dimensional structural order to smectic G with additional 3-dimensional structural order and is characterised by the absence of swift distortions (reflecting confined molecular positions in the hexagonal lattice). The smectic F to smectic G transition involves a change of the environment of bond orientational order from 2-dimensional positional correlations to 3-dimensional ones, possibly involving a first order transition.

In this paper we report on density and DSC investigations of N(p-n-decyloxybenzylidene)p-n-tetradecylaniline, viz. 10O.14. The pressure dependence of the IF and FG transition temperatures is estimated from the density and DSC data.

Experimental

The compound 10O.14 was synthesized from the respective benzaldehyde and alkyl aniline, and thermal microscopy (TM) was carried out as reported in [4]. The density investigations were carried out using a bicapillary pyknometer [5]. The accuracy in measuring the density is ± 0.1 kg m^{-3}, and the temperature of the system is accurate to ± 0.1 °C. The cooling rate during the density measurements was 1 °C per hour. The DSC was carried out with a Perkin-Elmer DSC-7 instrument. The molecular formula of the compound

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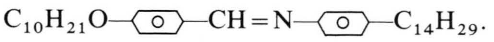
Reprint requests to Dr. N. V. S. Rao, Centre for Liquid Crystal Research and Education, Faculty of Physical Sciences, Nagarjuna University, Nagarjuna Nagar-522 510.

Table 1. Transition temperatures, enthalpy values and pressure dependence of T_c of the compound 10O.14.

Method	IF Transition	FG Transition	G-Solid
Thermal microscopy	83.5 °C	83.2 °C	68.5 °C
Density	83.3 °C	82.0 °C	
DSC	83.15 °C	81.37 °C	
ΔH, J/mol	9323	5105	
$\mathrm{d}T_c/\mathrm{d}p$, K/kbar	47.24	1.67	

10O.14 is



The transition temperatures obtained from TM, DSC and density jumps, the enthalpy (ΔH) and the estimated pressure dependence of the transition temperatures ($\mathrm{d}T_c/\mathrm{d}p$) are presented in Table 1.

Results and Discussion

The variation of the density (ϱ) and the volume expansion coefficient (α) with temperature (T) of the compound 10O.14 is illustrated in Figs. 1 and 2, respectively. The estimated increment in molar volume per methylene unit in isotropic liquid 10O.14 at $T_{\mathrm{IF}} + 5$ °C as compared with the compounds of the 9O.m series [6] is found to be $15.32 \cdot 10^{-6}$ cm^3 mol^{-1}, in agreement with the reported values for the compounds with $n = 4, 5, 6, 7$ and 9 of the nO.m series [6–9].

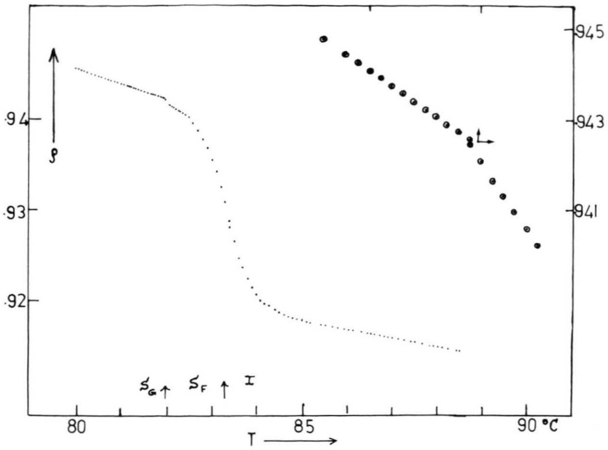


Fig. 1. Density (ϱ in g/cm^3) versus temperature (T in °C) of the compound 10O.14 with a blow up at the FG transition.

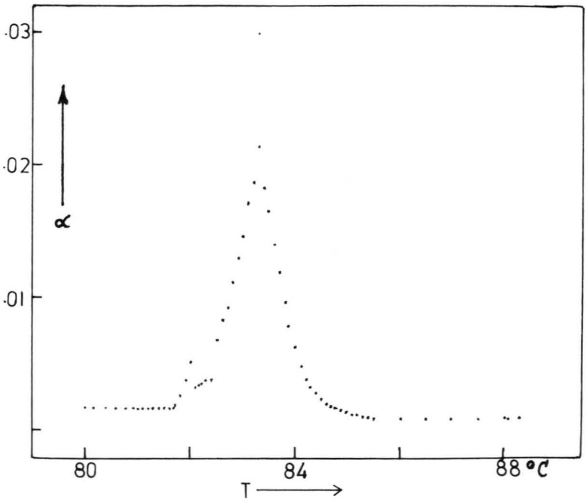


Fig. 2. Volume expansion coefficient (α) versus temperature (T in °C) of the compound 10O.14.

Isotropic-Smectic F (IF) Transition

The IF transition is accompanied by a large density jump of 2.14% and a thermal expansion coefficient peak of $295.4 \cdot 10^{-4}$ °C^{-1}, showing that the transition is of first order. The density jump is larger than any other reported jump across IN or IA transitions [6, 7] in nO.m compounds or IC transitions in TBAA compounds and esters [10, 11]. This large jump is due to the growth of bond orientational order rather than the growth of one-dimensional order.

It is apparent from Fig. 1 that the density increases linearly in the isotropic phase ($\mathrm{d}\varrho/\mathrm{d}T = -9.36 \cdot 10^4$ °C^{-1}), while it increases nonlinearly in the vicinity of the IF transition. The fluctuation dominated non-linear region (FDNLR), which covers 2.2 °C on the high temperature side (isotropic phase) of the IF transition, is larger than that across the nucleation growth of the IA transition reported for other compounds [6]. The observed nonlinear density variation on the isotropic side can be envisaged as the volume swept by the molecules possessing hindered rotational degrees of freedom under the influence of the smectic-F phase, i.e. in the vicinity of a phase transition the volume occupied by a molecule with minimum potential energy is influenced by the competitive growth of molecular crystalline order and the lower temperature phase. When the molecules at a phase boundary are subjected to swift distortions, they will attain a denser environment beause of the closer packing in the lower temperature phase. In the light of the data on nucleation growth of the isotropic-smectic A transition [6] (where the onset of simultaneous orientational and translational order parameters is reported), the growth of the positional correlations of the smectic-F phase (in the isotropic liquid), can be traced to a first approximation through the observed density increment in the non-linear region for $T > T_{\mathrm{IF}}$. Even though the density increment in the FDNLR (when the isotropic linear contributions are subtracted) can account for the growth of hexagonal smectic F positional correlations, the density data by themselves may not be able to resolve their contributions independently on an absolute scale (due to the onset of simultaneous a) orientational, b) translational and c) tilt order parameters). Further, a comparison between the nucleation growth IA transition [6] (involving simultaneous growth of both order parameters rather than one after the other) and the IF transition is made to support the estimate of relative growth of hexagonal order from density data.

The observed density data in the fluctuation dominated non-linear region (FDNLR) for $T > T_{\mathrm{IF}}$ is fitted to a six-fold temperature dependence in the following way:

$$(\Delta\varrho)_{\mathrm{Hex}} \propto \exp[\beta \times \Delta T], \tag{1}$$

i.e.

$$(\Delta\varrho)_{\mathrm{Hex}} = [(\delta\varrho_{\mathrm{IF}}) - (\delta\varrho)_T],$$

where

$$\begin{aligned}
(\delta\varrho)_{\mathrm{IF}} &= (\varrho_{\mathrm{IF}} - \varrho_{\mathrm{IF-extp}}),\\
(\delta\varrho)_T &= (\varrho_{\mathrm{T}} - \varrho_{T\mathrm{-extp}}),\\
\varrho_{\mathrm{IF-extp}} &= [\varrho_{\mathrm{IF+5}} + \{(\mathrm{d}\varrho/\mathrm{d}T)_{\mathrm{iso}} \times (T_{\mathrm{IF+5}} - T_{\mathrm{IF}})\}],\\
\varrho_{T\mathrm{-extp}} &= [\varrho_{\mathrm{IF+5}} + (\mathrm{d}\varrho/\mathrm{d}T)_{\mathrm{iso}} \times (T_{\mathrm{IF+5}} - T)],\\
\Delta T &= (T - T_{\mathrm{IF}}),
\end{aligned}$$

ϱ_{IF} being the observed density at the IF transition temperature, ϱ_T the density at any reference temperature T in the fluctuation dominated non linear region for $T > T_{\mathrm{IF}}$ ($\approx 2.2\,^{\circ}\mathrm{C}$), $\varrho_{\mathrm{IF+5}}$ the density in the isotropic liquid state (which is found to be in good agreement with estimated molar volume), $\mathrm{d}\varrho/\mathrm{d}T = -9.62 \cdot 10^{-4}\,^{\circ}\mathrm{C}^{-1}$ the observed equilibrium density increment with temperature in the isotropic state to account for the subtracted isotropic (linear) contributions and $\beta = 6\,b$ the exponent to characterise the exponential growth of hexagonal positional order tuned by b value.

Density data in the FDNLR of the IF transition, fitted to (1) for $T > T_{\mathrm{IF}}$, yielded $b = 0.75 \pm 0.001$, characterising the growth of six-fold hexagonal symmetry of the smectic F phase with exponential growth of positional correlations. The magnitude of b fitted to (1) reflects the rate of growth of each of the six simultaneous equivalent molecular volumes with triangular cross sectional area. Thus b is the characteristic value relating the packing fraction (0.73) of the solid state hexagonal system [12] to the relative density increments. The goodness of the fit is demonstrated by a χ^2-test. The relevant value of χ^2 is $3.061 \cdot 10^{-4}$, whose p value is found to be larger than 0.99.

The pressure dependence of the IF transition temperature ($\mathrm{d}T_{\mathrm{IF}}/\mathrm{d}p$), estimated from the density and DSC data using the Clausius-Clapeyron equation is 47.2 K/k bar. The magnitude of this T_{IF} value implies a steeper interface on the P-T plane and is of the same order as the reported values [7] at the AB transition in the lower nO.m homologues. The comparison of the relative packing of molecules between the isotropic and smectic F phases on either side of the IF transition can not be carried out since the observed density

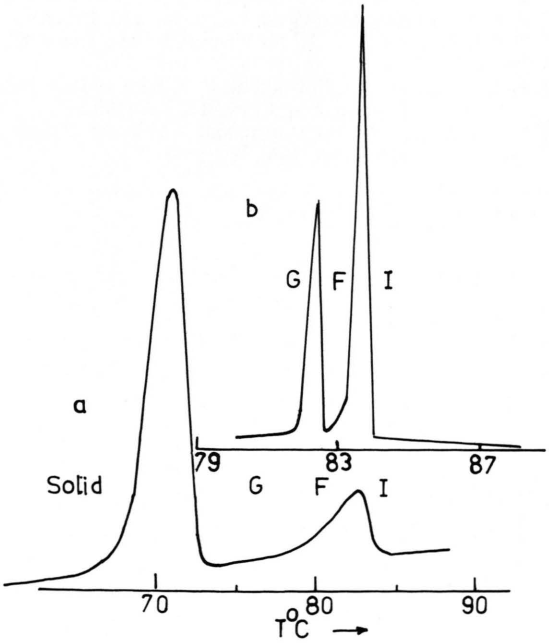


Fig. 3. DSC charts for the compound 10O.14. (a) scan rate 5 K/min, (b) 0.2 K/min.

in FDNLR on the lower temperature side of the transition does not obviously correspond to the equilibrium smectic F phase (Figure 2). This may be due to the small thermal range of the smectic F phase before the FG transition, since its fluctuations contribute to the premature three dimensional smectic G fluctuations to result in the observed larger density jump as an abortive settlement of smectic F swift distortions.

Smectic F – Smectic G (FG) Transition

The FG transition is accompanied by a small density jump of 0.04% and a volume expansion coefficient peak of $50.87 \cdot 10^{-4}\,°\mathrm{C}^{-1}$, showing that the transition is of weak first order. The DSC measurements [4] with 5 deg. per min. scanning rate could not resolve the weak first order FG transition peak (Figure 3a). The shoulder of the DSC peak on the lower temperature side of the IF transition extended for 1.3 °C (below the IF transition peak) before reaching the base line. The smeared region in DSC chart cannot distinctly distinguish the IF and FG phase transitions when separated by a narrow thermal range of the smectic F phase. However, the DSC run with a scan rate of 0.2 °C per min. has yielded resolved transition peaks for the IF and FG transitions (Figure 3b). Though, the FG transition is an expected first order transition, the density results apparently suggest a weak first order, and these results are in agreement with the reported [1] high resolution techniques at FG transitions.

Acknowledgements

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