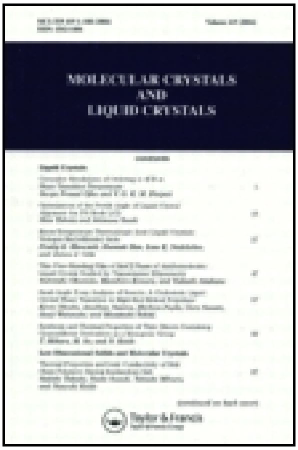

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Phase Transition Studies in 40.12

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Phase Transition Studies in 40.12

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The compound N(*p-n*-butyloxy benzylidene) *p-n*-dodecyl aniline, 40.12, a higher homologue of 4O.m in the nO.m series, exhibits a phase sequence of NAB. The synthesis and the characterization of the phases are presented. The nature of the phase transitions are determined from the temperature dependence of density and ultrasonic velocity. The nematic–smectic A transition is found to be a weak first order tending to a second order. The results are discussed in the light of the available data on other nO.m compounds.

INTRODUCTION

The liquid crystalline N(*p-n*-alkoxy benzylidene) *p-n*-alkyl aniline homologous series which are known as nO.m (n = alkoxy, m = alkyl) compounds are subjected to thorough investigation[1–8] for their physical properties in recent years as they exhibit abundant and subtle polymesomorphism. These comounds exhibit various smectic phases and a nematic phase. A study of mesomorphic phase transitions *i.e.*, characterization of phases by thermal microscopy, determination of the nature and associated physical changes of a phase transition by x-ray,[9] density[10–12] and ultrasonic velocity[13] studies give the necessary information regarding the phase identification, nature of the transition and molecular packing.

The continuous rotational symmetry of isotropic phase is broken at the isotropic–nematic (IN) transition. This IN transition which involves a change of a disordered phase into a long range orientationally ordered phase is a universally accepted first order phase transition. The nematic–Smectic A (NA) phase transition characteristics were explained on the basis of its proposed resemblances with the λ-transition of He-4. The NA transition involves the growth of a one-dimensional density wave in a three-dimensional fluid with the density wave growing along nematic director. Different theoretical approaches[14–25] proposed that the NA transition may be first order or a second order or an existence of a tricritical point (TCP) in binary mixtures. The experimental investigations revealed that the order of NA transition is first order[26–30] in some compounds, second order[31–35] in some other compounds while it is weak first order[36] tending to second order in few other compounds. Recent experimental results revealed that the tricritical point which defines the point separating the first order and second order NA transition, does exist in binary mixtures.[37–43] However, the body of the data provides no clear information re-

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garding the determination of the order of the transition or its dependence on nematic and smectic ranges or the molecular length to layer spacing ratio. These nO.m compounds povide an opportunity to study the NA transition in detail to infer the presence of above factors. The smectic A–Smectic B (AB) is a clear first order transition with the setting of characteristic three dimensional long range positional ordering in the smectic-B phase.

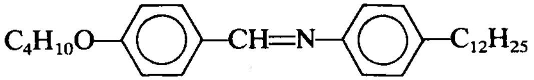
Extensive studies are carried out in N(*p*-*n*-butyloxy benzylidene) *p*-*n*-alkyl aniline (40.m) homologous series[31,33,44–46] by various experimental techniques and NA transition was a second order transition except in the case of 40.10 which exhibits a questionable first order NA transition leading to a second order. We present here the density and ultrasonic velocity results of 40.12, a higher homologue of 4O.m series, in an attemt to understand the nature of the NA transition in particular along with IN and AB transitions.

EXPERIMENTAL

40.12 was prepared by condensation of *p*-*n*-butoxybenzaldehyde (0.1 mole) and *p*-*n*-dodecylaniline (0.1 mole) in refluxing absolute ethanol in the presence of few drops of glacial acetic acid. After refluxing the reactants for four hours, the solvent was removed by distillation under reduced pressure. The crude 40.12 was recrystallised in ethanol in cold to give pure compound. The density and ultrasonic velocity measurements were carried out following the procedure reported[28] earlier. The temperature accuracy is ± 0.1°C. The density measurement has an absolute accuracy of ± 0.1 Kg.m^{-3}. The ultrasonic velocity measurements are accurate to 0.4 m·S^{-1}. Various phases and phase transition temperatures are identified and characterized with the help of a Hertel–Reuss (Super pan II) polarizing microscope attached with a hot stage. The phase transition temperatures are further confirmed by a Perkin Elmer DSC-4 instrument.

RESULTS AND DISCUSSION

The phase transition temperatures and characterization of the phases are not reported earlier to our knowledge. Thermal microscopy indicated three enantiotropic liquid crystalline phases *Viz.*, nematic, smectic A and Smectic B with their characteristic[47,48] textures. The molecular formula and the transition temperatures are given as



$$\text{Solid} \xleftrightarrow{39^\circ\text{C}} \text{Smectic B} \xleftrightarrow{51.9^\circ\text{C}} \text{Smectic A} \xleftrightarrow{69.5^\circ\text{C}} \text{Nematic} \xleftrightarrow{77.5^\circ\text{C}} \text{Isotropic}$$

The temperature dependence of density (ρ), ultrasonic velocity (V) and derived parameters *Viz.*, thermal expansion coefficient (α) adiabatic compressibility (β_{ad})

molar sound velocity $(R_n)^{49}$ and molar compressibility $(A_w)^{50}$ are illustrated in Figures 1, 2, 3, 4 and 5 respectively. The molar volume in the isotropic phase at $(T_{NI} + 5)$°C is 452.39×10^{-6} m^3 mol^{-1}. The increment per methylene group from 40.4 to 40.12 in isotropic liquid phase at $(T_{NI} + 5)$°C is 16.9×10^{-6} m^3 mol^{-1}. This is in reasonable agreement with reported values of 16.4×10^{-6} m^3 mol^{-1} to 17.2×10^{-6} m^3 mol^{-1} for the methylene group contribution of normal isotropic liquids. Density and ultrasonic velocity increase linearly with decreasing temperature in all the phases except in the vicinity of a phase transition. The molar compressibility (A_w) value $(250.7 \times 10^{-31/7}$ $m^{20/7}$ $Kg^{1/7}$ $S^{-2/7})$ computed from the experimental results in the isotropic phase is found to be in good agreement with the theoretically estimated value of $250.9 \times 10^{-31/7}$ $m^{20/7}$ $Kg^{1/7}$ $s^{-2/7}$ from the bond addivity data.[51] However, estimated molar sound velocity (R_n) at this temperature differs from the theoretical value by 3%. The increase in ultrasonic velocity with decreasing temperature is due to the increase of intermolecular potential which results as a consequence of decrease in intermolecular distance.

A sudden jump of density (0.35%) and an ultrasonic velocity dip (5.5 m S^{-1}) are observed at IN transition. Further, a thermal expansion coefficient maxima of 16.0×10^{-3} $°C^{-1}$ across this transition confirms the first order nature of IN transition. A larger value of the thermal expansion coefficient in nematic phase $(14 \times 10^{-4}$ $°C^{-1})$ than in the isotropic phase $(9.5 \times 10^{-4}$ $°C^{-1})$ indicates an increase in the molecular packing in the nematic phase and the accompanying growth of long range orientational order from the completely disordered molecular arrangement of isotropic phase. The pretransitional effects[52] which are observed

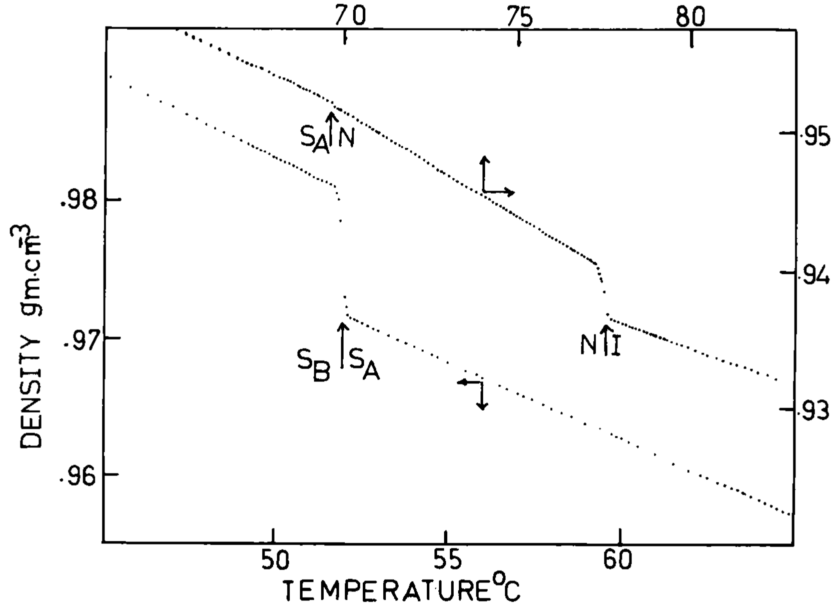


FIGURE 1 Density variation with temperature in the isotropic, nematic, smectic A and Smectic B phases of 40.12.

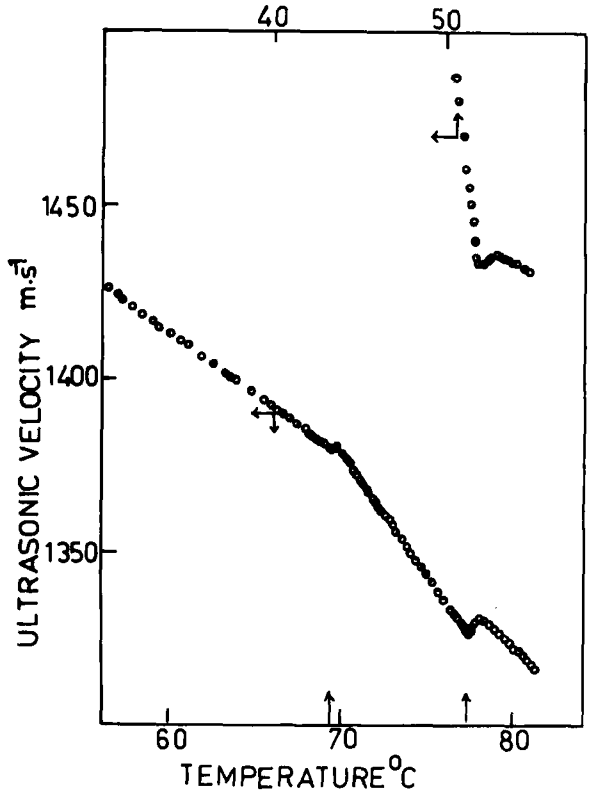


FIGURE 2 Ultrasonic velocity variation with temperature in the isotropic, nematic, smectic A and smectic B phase of 40.12.

for a thermal range of 3.5°C above the IN transition temperature in isotropic phase can be better explained from Frenkel's Heterophase fluctuation theory.[53] This pretransitional behavior is apparent from the temperature dependence of molar compressibility and molar sound velocity in the isotropic phase.

The nematic–smectic A (NA) transition is accompanied by a small jump in density (0.02%), a thermal expansion coefficient peak of 2.9×10^{-3} °C^{-1} and a shallow ultrasonic velocity dip of 0.9 m S^{-1}.

In the early 1970s' McMillan[15] and Kobayashi[14] basing on the mean field calculations predicted that the NA transition should be first order for $M = 0.87^{37}$. However, later studies inferred that McMillan's theory predicts the right total enthalpy when pretransitional contributions are included.

de Gennes[16] had proposed the NA transition as second order assuming the superfluid analogy in S_A phase which develops from nematic phase with the decreasing temperature. However, the experimental situation differs from de Gennes' proposal. The observed parameters *Viz.*, anisotropic gauge and barelengths, elastic free energies etc., deviated from the theory. Moreover, the coupling of smectic A density wave with orientational fluctuations and the decay in the smectic A translational periodic ordering are the new parameters introduced across the NA transition.

Alben[17] predicted a NA tricritical point (separating the first order and second order transitions) for a binary mixture (whose components individually exhibit first and second order transitions) when the average chain length of binary mixture corresponds to non-ordering field fluctuations and the nematic order parameter is the non-ordering density wave. Our results conclusively show that the NA transition in 40.12 is weak first order. The small density change between the nematic and smectic A phase does not however correspond to a step function; instead an almost linear behavior with a finite slope is observed (Figure 3—inset). Moreover, visually the two phase coexistence *i.e.*, floating of nematic phase over the smectic A phase was observed for a temperature range of 0.1°C. We believe that this temperature range may probably be smaller with high resolution experiments. Although it is conceivable that impurities can convert an otherwise second order transition into a first order transition, there is absolutely no reason to believe that this effect is occurring here. For example, the complete absence of pretransitional phenomena expected for second order transition weigh heavily against such hypothesis. The ahsence of pretransitional phenomena to a lesser extent in refractive index (unpublished results) and ultrasonic velocity (Figure 2 and the derived parameters Figures 4 and 5) variation with temperature support the hypothesis of weak first order transition. The thermal expansion coefficient variation with temperature (Figure 3—inset) precludes the possible pretransitional effects. The density change per degree rise of temperature either in the nematic or in the smectic A phases is much smaller than the density change across the NA transition.

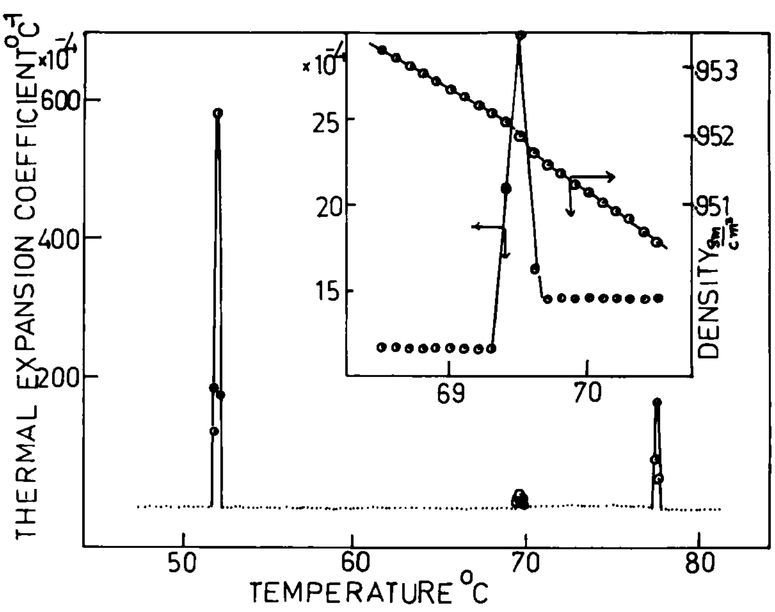


FIGURE 3 Thermal expansion coefficient variation with temperature in nematic, smectic A and smectic B phases of 40.12.

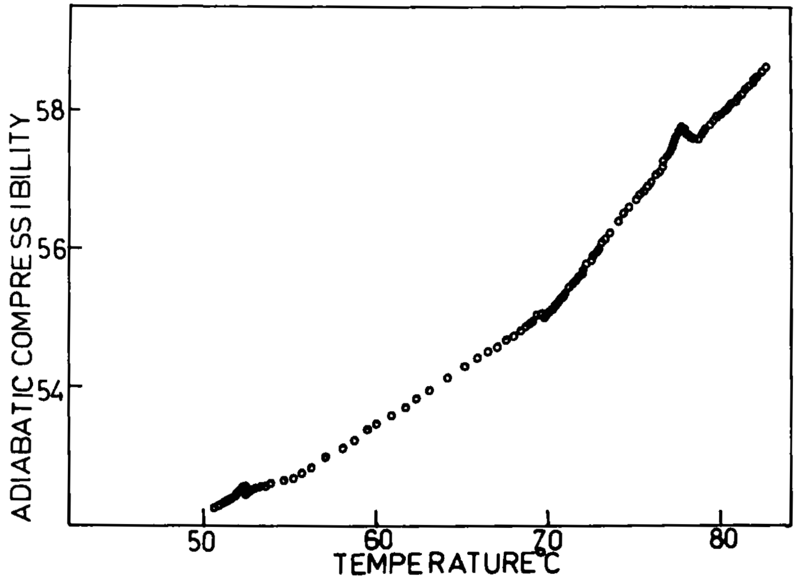


FIGURE 4 Adiabatic compressibility (β_{ad} in 10^{-3} m $Kg^{-1}s^{2}$) variation with temperature in nematic, smectic A and smectic B phases of 40.12.

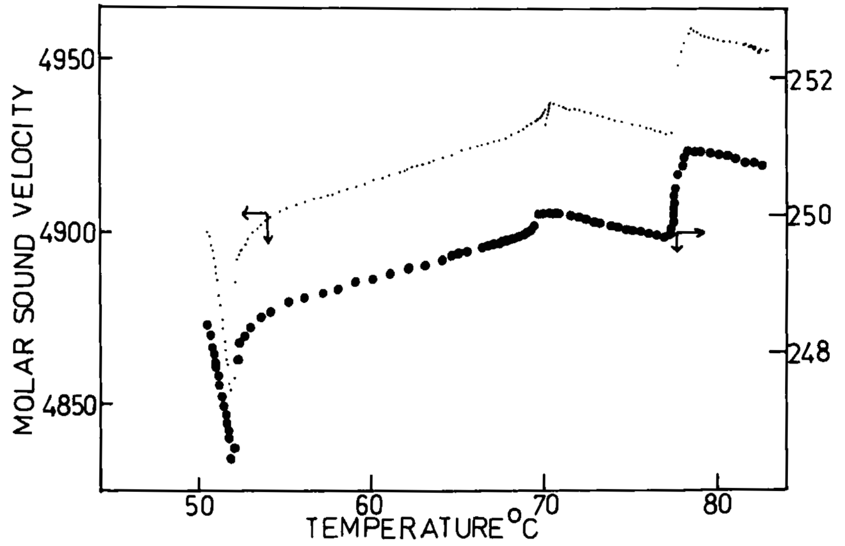


FIGURE 5 Molar sound velocity (●—●—●) $R_n \times 10^{-6}$ $m^{10/3}$ $S^{-1/3}$ and Molar compressibility (●—●—●). $A_w \times 10^{-31/7}$ $m^{20/7}$ $Kg^{1/7}$ $s^{-2/7}$ variation with temperature in 40.12.

Further support for a weak first order is as follows.

The T_{NA}/T_{NI} value (0.977) for the compound 40.12 is above the observed value reported for 40.6 + 60.4 (T_{NA}/T_{NI} = 0.955) and 80.3 + 20.3 (T_{NA}/T_{NI} = 0.96) mixtures.[37] Pisipati *et al.* reported a weak first order NA transition in 50.8 having an identical value of T_{NA}/T_{NI} = 0.977. Due to the presence of a large nematic thermal range of 8°C the orientational order in nematic phase is saturated near the NA transition, thereby leading to the arrest of nematic orientational fluctuations, leaving behind the newly growing translational periodic order of S_A phase to determine the NA transition either to be weak first order or a second order transition. The results suggest a weak first order NA transition and are in agreement with the theoretical prediction of Halperin and Lubensky.[18] The change from an opaque nematic phase to translucent S_A phase is observed visually which is due to the development of aditional periodic one-dimensional translational ordering.

A tricritical point differentiating the first order and second order in the binary mixtures of 80.3 + 20.3 for a value of $T_{NA}/T_{NI} \simeq 0.96$ was first reported by Johnson *et al.*[37] Recently observed results inferred the tricritical points in 60.4 + 40.6[43] mixtures and 40.8 + 60.8[42] mixtures at $T_{NA}/T_{NI} \simeq$ 0.955 and 0.978 respectively. These values are lower than the values of $T_{NA}/T_{NI} \simeq$ 0.992 and 0.984 (in other homologous series) observed for nCB and $\bar{n}$S5 mixtures respectively. Hence, we believe that these observations confirm that the NA transition in 40.12 to be a weak first order tending to a second order nature.

However, it must be mentioned here that some compounds *Viz.*, 40.12, 50.8 and 50.10 or 50.12, 60.4 and 70.5 or 40.10 and 70.1 possessing an almost identical nematic thermal ranges and the McMillan parameter values (T_{NA}/T_{NI}) did exhibit different orders of the NA phase transition *i.e.*, 50.12 exhibited second order while 60.4 and 70.5 exhibited first order phase transitions. It implies that the nematic thermal range is ineffective in deciding the order of the NA transition. Furthermore, the compounds 40.4,[44] 40.6, 40.7 and 40.8 exhibit second order NA transition while all compounds studied in the 60.m and 70.m homologous series exhibited a first order transition. Hence, it is apparent from these results that the alkoxy chain rather than the alkyl chain, plays a predominant role in deciding the nature of NA transition.

The crystalline smectic B possesses long range three dimensional order and positional correlations of the hexagonal in plane packing of the molecules, as well as the layer stacking. Transient transition bars are observed across the S_A–S_B transition followed by a fan texture with reduced number of discontinuities characterizing the phase as crystalline S_B phase. The S_A–S_B transition involves a change from positional disorder to positional order. The large density increase between S_A and S_B phases is not strictly a step function, but rather a linearly increasing one from S_A phase to S_B phase. This indicates the presence of two phase coexistence causing the broadening of transition. The broadening is explained as due to a two phase coexistence which occurs commonly and does not require pretransitional effects. It is possibly the transition from positionally disordered molecular arrangement in S_A layers to the ordering in S_B phase might be the origin of the two phase coexistence. The large density jump (0.89%) an ultrasonic velocity dip (2.5 m S^{-1}) and a large thermal expansion coefficient maxima of value 58×10^{-3} °C^{-1} indicate the S_A–S_B transition as first order. The ultrasonic velocity which is linear in the S_A phase shows an anomaly at S_A–S_B transition and steeply shoots up in S_B phase.

Acknowledgments

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