Density, Refractive Index and Ultrasonic Velocity Studies Involving N-(p-n-Pentyloxybenzylidene)-p-n-octylaniline

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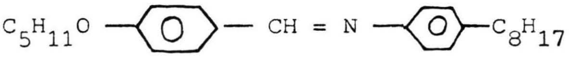
The density, refractive index and ultrasonic velocity dependence on temperature for N-(p-n-pentyloxybenzylidene)-p-n-octylaniline, 50.8, is presented. The compound 50.8 exhibits smectic-B, smectic-A and nematic phases between the solid and isotropic liquid phases. The nematic-isotropic and smectic A-smectic B phase transformations are found to be first order. The interesting smectic A – nematic transformation is confirmed from the results to be second order, although the thermal expansion coefficient and reported enthalpy data had suggested a weak first order transition. The computed adiabatic compressibility, β_{ad}, molar sound velocity, R_n, and molar compressibility A_w are presented.

Introduction

There is not yet a theoretical and experimental consensus about the critical behaviour at the nematic (N) to smectic-A (S_A) phase transition in liquid crystals. Lubensky [1] has critically reviewed the current status of the theory of the N–A transition and made comparisons with experiment, while Johnson [2] discussed the N–A tricritical point extensively and concluded that a careful study of critical exponents in homologous series and appropriate mixtures that cover a wide range of values of (T_{NA}/T_{NI}) is needed to lead to a concurrent theoretical and experimental situation. During the last few years extensive research by different methods for two homologous series has been focussed upon the S_A–N transition [3, 4]. The methods employed include X-rays, scanning calorimetry, light scattering, thermal microscopy, density, ultrasonic velocity etc. The compounds involved are N-(p-n-alkoxybenzylidene)-p-n-alkyl anilines [4] and p-n-alkyl or alkoxy-p′-cyanobiphenyls [3]. The N-(p-n-alkoxybenzylidene)-p′-n-alkylanilines (hereafter referred as n0.m compounds where n = alkoxy group and m = alkyl group) exhibit complex mesomorphism. They are highly susceptible to humidity and exposure to atmosphere. However they can be obtained in a pure form and detailed studies of phase transitions by different techniques are reported [5, 6]. Density, ultrasonic velocity, thermal microscopy and refractive index studies did yield interesting results on some of the compounds in our laboratory [4]. Recent studies on 40.8 and 40.7 at MIT [6, 7] indicated second order N–S_A transition using heat capacity, high resolution X-ray and light scattering methods. However our results on 50.4, 60.4, 70.4 and TBBA indicated first order N–S_A transition. In continuation of these results we carried out similar studies on 50.8 which exhibits interesting mesophases. 50.2 exhibits highly ordered S_G and nematic phases, 50.4 exhibits S_G, S_A and nematic phases while 50.6 exhibits S_G, S_F, S_B, S_C, S_A and N phases. The compound 50.8 exhibits only a monotropic S_G and enantiotropic S_B, S_A and N phases. The phase transition temperatures observed by density, ultrasonic velocity and refractive index studies are found to be compatible with the thermal microscopic and literature data [8]. The structural formula and transition temperatures are presented below:



$$\begin{tikzcd}
\text{Solid} \arrow[r, "43.5\,^{\circ}\mathrm{C}"] & \text{Smectic B} \arrow[r, shift left, "52.2\,^{\circ}\mathrm{C}"] \arrow[d, "28\,^{\circ}\mathrm{C}"] & \text{Smectic A} \arrow[l, shift left] \arrow[r, shift left, "68\,^{\circ}\mathrm{C}"] & {} \arrow[l, shift left] \\
& \text{Smectic G} \arrow[ul, "\sim 10\,^{\circ}\mathrm{C}"] & \text{Nematic} \arrow[r, shift left, "76\,^{\circ}\mathrm{C}"] & \text{Isotropic} \arrow[l, shift left]
\end{tikzcd}$$

Experimental

50.8 is prepared by condensation of p-n-pentyloxybenzaldehyde (0.1 mole) and p-n-octylaniline (0.1 mole) in boiling absolute ethanol in the presence of a few drops of glacial acetic acid. After re-

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fluxing the reactants for four hours the solvent is removed by distillation under reduced pressure, and later the pure compound is recrystallised from absolute ethanol in the cold. The molar volume and ultrasonic velocity measurements are carried out by a procedure similar to that reported earlier [4]. The refractive indices are measured with a modified laboratory spectrometer [9]. The temperature accuracy in all the experiments is ±0.1 °C. The density measurements are accurate to ±0.0001 gm/cm^3. The ultrasonic velocity measurements are accurate to ±0.1% while the refractive index measurements are accurate to 0.0005.

Results and Discussion

The variation of the density and the ultrasonic velocity with temperature is illustrated in Figs. 1a and b, and the variation of the refractive index with temperature for different spectral regions in Figure 2. The jump in density and refractive index and the anomalous dip in the ultrasonic velocity at the N–I transition confirmed it to be first order. The variation of the thermal expansion coefficient $\alpha = \mathrm{d} \ln V_\mathrm{m}/\mathrm{d}T$, where V_m = molar volume, with temperature is shown in Figure 3. It also supports the first order nature of the transition. The jump in molar volume at the N–I transition is $(\Delta V_\mathrm{m}/V_\mathrm{m}) = 0.25\%$; pretransitional effects are found to occur in the nematic region. The anomalous behaviour in the ultrasonic velocity ranges over 1.2 °C, while the anomalous decrease in ultrasonic velocity is 1.17% in comparison with the normal temperature dependence. All these results are compatible with data reported in literature [4, 10]. The jump in refractive index, i.e. n_iso to n_e or n_0, is high for blue light compared to the other spectral regions.

As to the order of the S_A–N phase transformation, the salient features observed are

a) a sudden jump in density is not observed in spite of repeated runs and different rates of cooling (0.3 °C to 2 °C per hour),

b) a dip in velocity of 4 m/sec is found and the anomalous decrease in ultrasonic velocity is $(\Delta V/V) = 0.3\%$,

c) the ordinary and extraordinary refractive indices show a continuous behaviour at the S_A–N transition,

d) the nematic-smectic A phase transformation is visible to the naked eye, i.e. a change from opaque nematic to translucent smectic A is observable,

e) the thermal expansion coefficient shows a peak $(22 \times 10^{-4}\,\mathrm{K}^{-1})$ with pretransitional effects on both sides of the transition temperature,

and indicate a weak first order or second order transition. It may however be argued that the peak is due to pretransitional effects at the transition, and only high resolution studies can distinguish weak first order and second order transitions. In view of the ultrasonic velocity and refractive index results, which support the density data, we conclude that this S_A–N transition is of second order. The calorimetric study [8] reported a transition enthalpy of 920 J/mole at this transition. This is higher than the

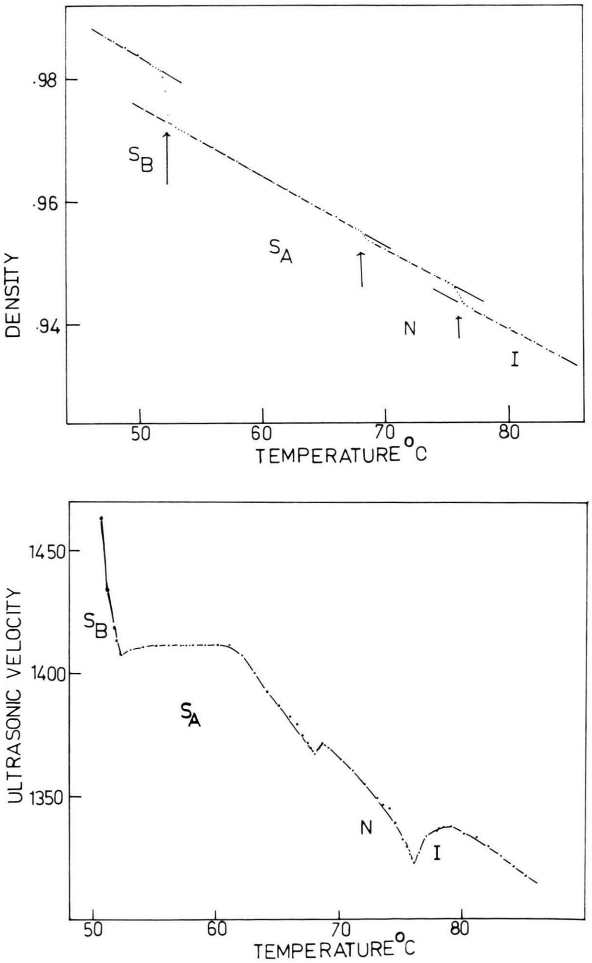

Fig. 1. Density (g/cm^3) and ultrasonic velocity (cm/sec) vs. temperature for 50.8 in its S_B, S_A, N and I phases.

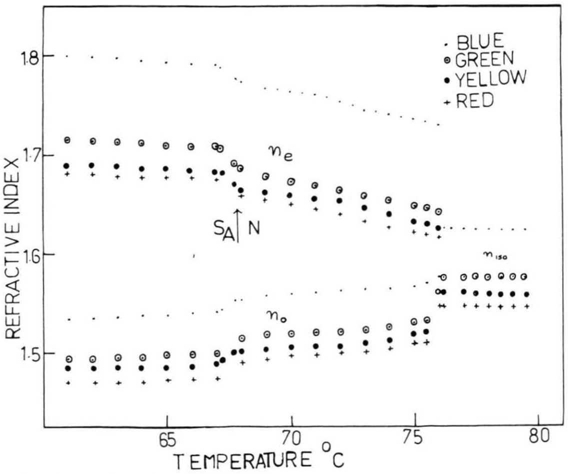

Fig. 2. Refractive indices vs. temperature for the nematic and smectic A phases of 50.8.

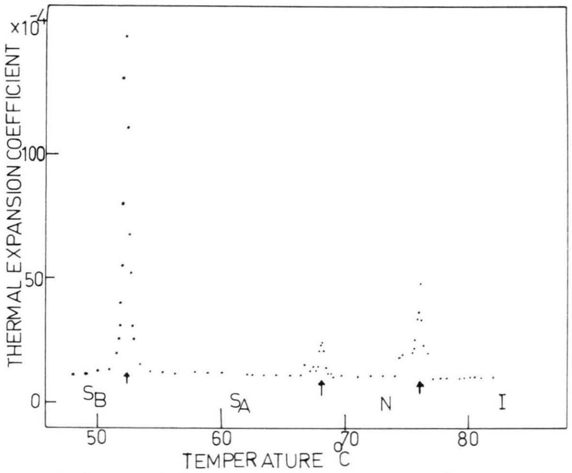

Fig. 3. Thermal expansion coefficient (K^{-1}) of 50.8 vs. temperature.

pretransitional heat of transition. Unless high resolution adiabatic scanning calorimetry is carried out the discrepancy cannot be explained.

The crystalline smectic B phase possesses long range three dimensional (3 D) order and positional correlations of the hexagonal in plane packing of the molecules, as well as of the layer stacking. We observed transition bars across the fans at the S_A–S_B transition followed by fans with a reduced number of discontinuities characterising this phase of 50.8 as crystalline smectic B. The smectic A–smectic B transition involves the development of in-plane order. Therefore the transition must be first order, and indeed our results conclusively show that in 50.8 the transition is strongly first order. The large density increase between the smectic A and crystalline smectic B phases does not however correspond to a step function; instead an almost linear behaviour with a finite slope is observed. This indicates the existence of an impurity broadened two phase region between 52 and 52.3 °C. Hence this broadening can be explained as being due to a two phase coexistence, which occurs commonly and does not require pretransitional effects. Moreover the transition from disordered molecular arrangement inside the layers of smectic A to the ordering in smectic B might be the origin of the two phase coexistence. 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 occuring here. For example the complete absence of pretransition phenomena expected for second or weakly first order transitions weights heavily against any such hypothesis. The jump at this transition is $(\Delta\varrho/\varrho) = 0.79\%$. The pressure dependence of the smectic A–smectic B transition temperature is estimated using the Clausius-Clapeyron equation $(\mathrm{d}T_t/\mathrm{d}P) = T_t(V/H)$; where T_t is the transition temperature, P the pressure, V_m the volume change associated with the transition and H the heat of transition. Using the V_m values from our experimental graph and the H values from the literature [9] the computed value of $(\mathrm{d}T_t/\mathrm{d}P)$ is 49.8 K/k bar.

The ultrasonic velocity, which is constant in the lower temperature region of the smectic A phase, shows an anomalous behaviour at the transition temperature and then suddenly shoots up in the S_B phase. It is apparent that this anomaly agrees with the density result and leads to the conclusion that the S_A–S_B transition is first order.

The adiabatic compressibility β_{ad}, molar sound velocity R_n and molar compressibility A_ω as displayed in Figs. 4 and 5 are computed using the relations

$$\beta_{ad} = v/V^2\,; \quad R_n = V_m V^{1/3}\,; \quad A_\omega = V_m \beta_{ad}^{-1/7}\,,$$

where v = specific volume, V = ultrasonic velocity and V_m = molar volume: The adiabatic compressibility shows pretransitional effects in the vicinity of all the phase transitions. The molar sound velocity R_n in the isotropic phase is $4452 \times 10^{-6}\,\mathrm{m}^{10/3}\,\mathrm{s}^{-1/3}$ and is found to be lower than the computed value of

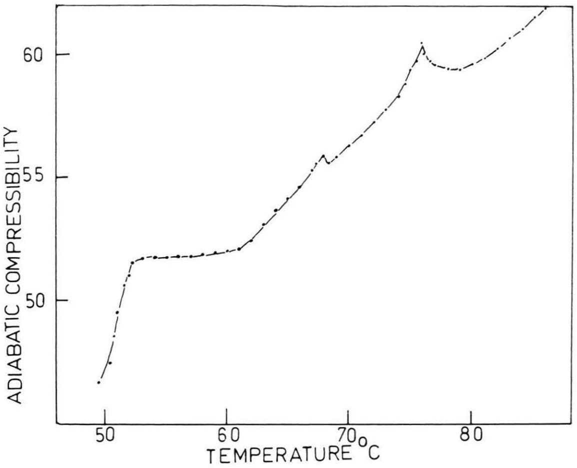

Fig. 4. Adiabatic compressibility β_{ad} (10^{-3} m kg^{-1} s^2) of 50.8 vs. temperature.

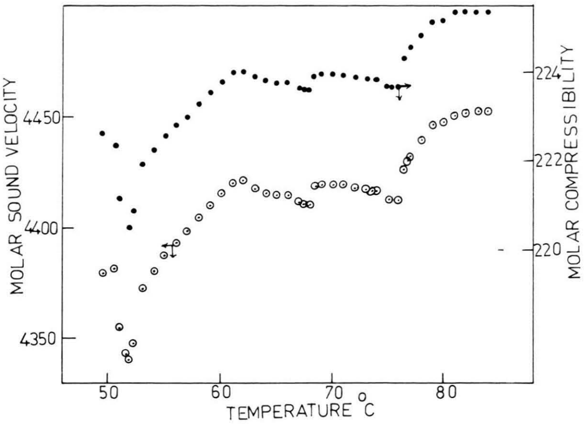

Fig. 5. Variation of molar sound velocity R_n (10^{-6} m$^{10/3}$ s$^{-1/3}$) and molar compressibility A_ω ($10^{-31/7}$ m$^{20/7}$ kg$^{1/7}$ s$^{-2/7}$) with temperature for 50.8.

4553 from Rao's atomic data [11]. All the transitions are indicated by minima, and pretransitional effects are found to be on the lower temperature side of the transition. Both molar sound velocity and molar compressibility are found to be constant in the nematic phase, while they steeply decrease with decreasing temperature in the S_A phase. The calculated value of the molar compressibility ($223.6 \times 10^{-31/7}$ m$^{20/7}$ kg$^{1/7}$ s$^{-2/7}$) from Wada's table [12] is slightly lower than the experimental value (225.4).

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