Specific Volume and Ultrasonic Velocity Studies of the Liquid Crystal N-(p-n-hexyloxybenzylidene)-p-n-butylaniline (H_xBBA)

L. V. Choudary, J. V. Rao, P. N. Murty, and C. R. K. Murty
Department of Physics, Nagarjuna University, Nagarjunanagar, A.P., India

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Specific volume and ultrasonic velocity measurements have been carried out on the liquid crystal N-(p-n-hexyloxybenzylidene)-p-n-butylaniline in the isotropic, nematic, smectic A, smectic B and smectic G phases. The variation of the specific volume with temperature shows that the corresponding transitions are of first order. Thermal expansion coefficients have been calculated for all the mesophases. The ultrasonic velocity variation with temperature confirms the transitions.

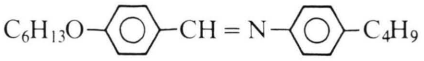
Introduction

Now a days liquid crystals are fascinating to many researchers because of their important technical applications and peculiar behaviour [1].

The N-(p-n-alkoxybenzylidene)-p-n-alkylanilines, though having a simple structure, exhibit a complex polymesomorphism. Existing controversies in this series [2–5] have induced us to reexamine the phase transitions of the liquid crystal N-(p-n-hexyloxybenzylidene)-p-n-butylaniline (H_xBBA). For our previous studies on liquid crystals cf. [6, 7].

Experimental

H_xBBA has been synthesized by condensation of p-n-hexyloxybenzaldehyde and p-n-butylaniline in refluxing ethanol by adding a few drops of acetic acid. After refluxing the reactants for four hours the solvent has been removed by distillation under reduced pressure. The transition temperatures of the purified compound as determined using a polarising microscope [8], have been formed to be



$$\text{Solid} \xleftrightarrow{32\,^\circ\text{C}} S_G \xleftrightarrow{57.0\,^\circ\text{C}} S_B \xleftrightarrow{59.4\,^\circ\text{C}}$$

$$S_A \xleftrightarrow{69.2\,^\circ\text{C}} \text{Nematic} \xleftrightarrow{78.8\,^\circ\text{C}} \text{Isotropic}\,.$$

The specific volume has been measured using a pyknometer of capillary bore 0.5 mm. The temperature was controlled within ±0.1 °C. The level of the liquid crystal has been read by a cathetometer of sensitivity 10 μm. The absolute error in the measurement of the specific volume was ±0.0001 cc/g.

The ultrasonic velocity was measured at 2 MHz using the ultrasonic interferometer UI 601 supplied by N.P.L. India. The temperature was controlled by a thermostated liquid flowing around the cell. The absolute error in the measurement of the ultrasonic velocity is estimated to be ±0.1%.

Results

The thermal expansion coefficient α was calculated from the formula

$$\alpha = \frac{1}{V_n}\left[\frac{\Delta V}{\Delta T}\right],$$

where $V_n = \frac{1}{2}(V_1 + V_2)$, $\Delta V = (V_2 - V_1)$ and $\Delta T = (T_2 - T_1)$, V_1 and V_2 being the molar volumes at the temperatures T_1 and T_2, respectively.

The variation of the specific volume with temperature is shown in Figs. 1 and 2, the thermal expansion coefficients at the transition temperatures are represented in Fig. 3 and the ultrasonic velocity variation with temperature is shown in Figure 4.

Discussion

In the smectic G phase the specific volume increases linearly with increasing temperature (cf.

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Figure 1). Near the smectic G–smectic B transition a jump in specific volume is observed. The jump in specific volume and high value of thermal expansion coefficient ($\alpha = 45.1195 \cdot 10^{-4}/°C$, cf. Fig. 3) indicate that this transition is of first order. Also in the smectic B phase the specific volume increases linearly with temperature and at the S_B–S_A transition a jump is observed. This jump in specific volume is greater than at any other transitions. Wigeleben et al. [9] have observed that also the jump in enthalpy at this transition is greater than at other transitions. The jump in specific volume, amounting to 0.399%, and the large value of α ($49.80 \cdot 10^{-4}/°C$) suggest that this transition as first order. This involves considerable change in the structure. In the smectic A phase the specific volume increases linearly with temperature and at the smectic A–nematic transition a jump in specific volume (0.2067%) is observed (cf. Figure 2). For this transition some controversies exist in the literature [10, 11, 12]. De Jeu from the heat of transition studies on di-n hexyl, heptyl and octyl azoxybenzenes found that the smectic A–nematic transitions are of first order, weakly first and second order, respectively [13]. The jump in specific volume suggests that this transition is also of first order. Flannery et al. [3] have also observed the same from their DSC measurements.

Also near the nematic–isotropic transition a jump in specific volume (0.3413%) is observed. The pretransitional effect observed on the lower side of this transition can be explained in the light of Maier Saupe's theory [14]. The breadth of the transition is 1.4 °C. The high value of the thermal expansion coefficient and the jump in specific volume show that this transition is of first order, as expected. Maier and Saupe [15] have given values of $A/KT_k V_{nk}^2$ and S_k versus $\Delta v_k/v_{nk}$, where S_k is an order parameter, A a characteristic constant of the substance, K Boltzmann's constant, T_k the transition temperature and V_{nk} the molar volume at the

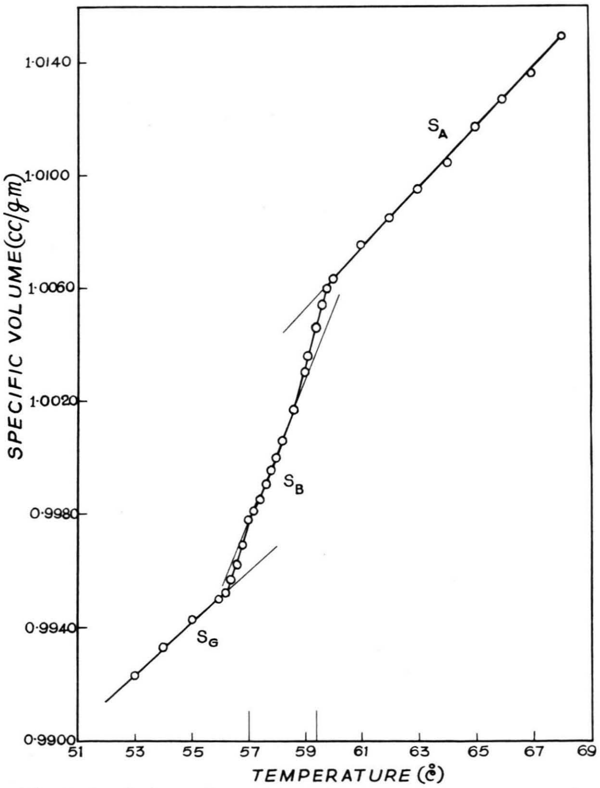

Fig. 1. Variation of specific volume with temperature in the S_G, S_B and S_A phases.

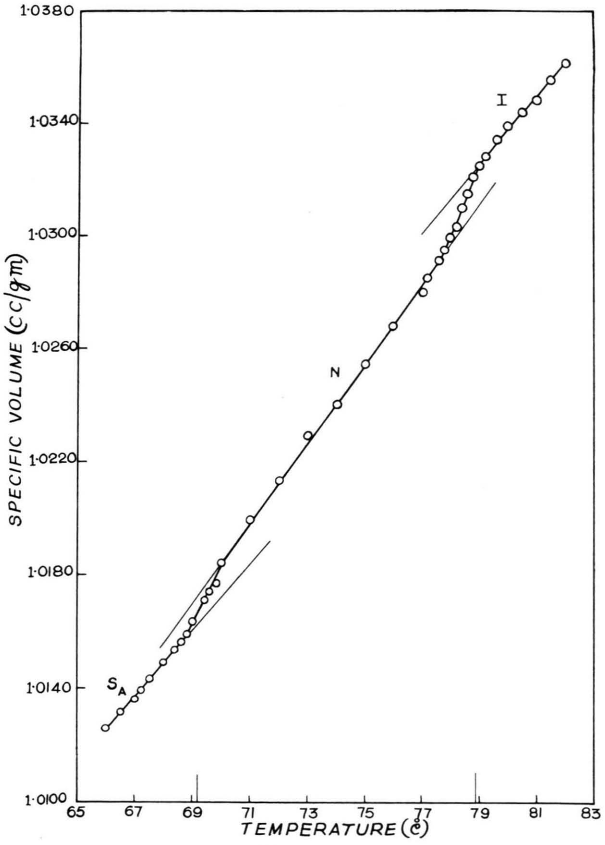

Fig. 2. Variation of specific volume with temperature in the S_A, Nematic and Isotropic phases.

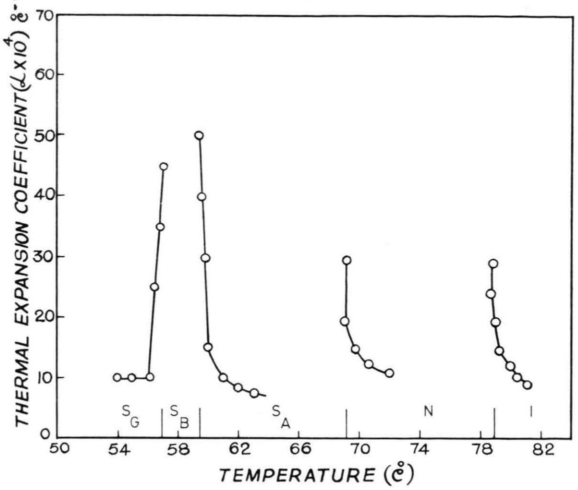

Fig. 3. Variation of Thermal expansion coefficients at the phase transitions with temperature.

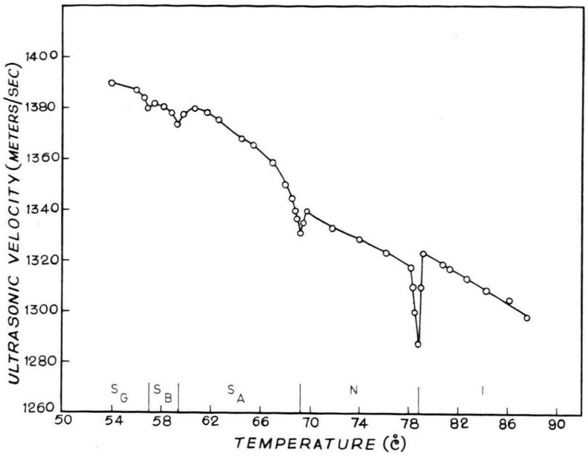

Fig. 4. Variation of ultrasonic velocity with temperature.

transition. Here Δv_k is the change in specific volume at the transition and v_{nk} the specific volume at the transition on the isotropic side. From our value $\Delta v_k/v_{nk} = 0.0034$ we found S_k and A to be 0.4425 and $26.87 \cdot 10^{-9}$ erg cm^6, respectively.

Figure 4 shows that the ultrasonic velocity generally increases with decreasing temperature. This is due to the decrease of the mean interparticle distance with decreasing temperature, which involves an increase in the interparticle forces [16]. Minima at the transitions and pretransitional effects on both sides of the transitions are observed. The latter can be explained on the basis of Frenkel's heterophase fluctuation theory [17]. The total interval of anamoulus change at the isotropic–nematictransition takes place in a temperature range of 1.2 °C. A dip in the velocity at the nematic–smectic A transition has also been reported by Bahadur [18] for OBT. At the $S_A - S_B$ and $S_B - S_G$ transitions the change in the ultrasonic velocity is very small compared to that at the isotropic–nematic transition. In the nematic phase, S varies from 0.2 to 0.8 and is temperature dependent. S varies from 0.8 to 0.95 in smectics and is less temperature dependent. This may be the reason for the small changes in the velocity at the nematic–smectic A and smectic–smectic transitions.

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