Specific Volume and Ultrasonic Velocity Studies of the Liquid Crystal N-(p-n-hexyloxybenzylidene)-p-n-butylaniline (H$_x$BBA)

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Z. Naturforsch. 38a, 762–764 (1983); received February 1, 1983

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$_x$BBA). For our previous studies on liquid crystals cf. [6, 7].

Experimental

H$_x$BBA 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

\[
\begin{align*}
\text{C}_6\text{H}_5\text{O} & \quad \text{CH} \quad \text{N} \quad \text{C}_4\text{H}_9 \\
\text{Solid} & \quad \text{S}_G \quad \text{N} \quad \text{S}_A \\
\text{S}_A & \quad \text{Nematic} \quad \text{Isotropic}.
\end{align*}
\]

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 $\alpha$ 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.
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 \( \alpha = 45.1195 \times 10^{-4} / ^\circ C \) 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 \( \alpha \) (49.80 \times 10^{-4} / ^\circ 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 \(^\circ C\). 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 \( AV_k/V_{nk} \), 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

![Figure 1](image1.png)

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

![Figure 2](image2.png)

Fig. 2. Variation of specific volume with temperature in the \( S_A \), Nematic and Isotropic phases.
transition. Here $\Delta V_k$ 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$^3$, 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 anamalous change at the isotropic–nematic transition 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 $S_A$–$S_9$ and $S_9$–$S_G$ 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.

Acknowledgements

L. V. Choudary is grateful to the electronics commission, New Delhi for providing him a fellowship. J. V. Rao and P. N. Murty are grateful to CSIR, New Delhi for financial assistance.