Specific Volume Studies on Some Nematic Liquid Crystals

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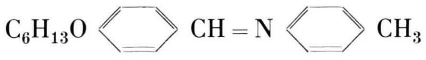
The temperature variation of the specific volume of two nematic liquid crystals (HBT and OBT) has been observed in both the nematic and isotropic regions. A sudden jump is observed in the vicinity of the nematic-isotropic transition indicating a first order phase transition. Pretransitional effects are found to occur only on the nematic side of the transition. This accords with the Maier-Saupe theory. Some parameters such as S_k, A, the adiabatic compressibility, the Rao number, and the van der Waals constant are also determined.

Now a days the liquid crystalline state is recognized as a true state intermediate between the crystalline solid and the isotropic liquid state[1–6]. Generally, the mesophase-isotropic phase transitions are regarded as of first order though some recent measurements on this transition show some second order admixture. Indeed, the cholestric and nematic liquid crystals exhibit the smallest first order transitions to the isotropic liquid known among pure compounds. In first order phase transitions a discontinuity or a steep change in specific volume is observed, while in second order transitions a point of inversion occurs (i. e. no discontinuity occurs in the first derivatives of Gibbs' free energy[7] at the transition).

This paper, dealing with specific volume measurements of two nematic liquid crystals, (p-n-hexyloxybenzylidene)-p-toluidine (HBT) and (p-n-octyloxybenzylidene)-p-toluidine (OBT), is part of our systematic study on liquid crystals[8–14].

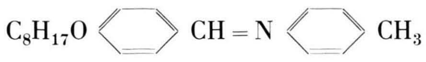
Both HBT and OBT were procured from *M/S* E. Merck (Germany) in pure form and were used as such. The transition temperatures were determined by means of a polarizing microscope and are listed below

1. HBT



$\text{Solid} \underset{52^\circ\text{C}}{\overset{54^\circ\text{C}}{\rightleftharpoons}} \text{Nematic} \overset{72.5^\circ\text{C}}{\rightleftharpoons} \text{Isotropic}$

2. OBT



$\text{Solid} \underset{68^\circ\text{C}}{\overset{68.6^\circ\text{C}}{\rightleftharpoons}} \text{Smectic} \overset{69.0^\circ\text{C}}{\rightleftharpoons} \text{Nematic} \overset{75.0^\circ\text{C}}{\rightleftharpoons} \text{Isotropic}$

The specific volume was measured by means of a sensitive pycnometer[11], which was placed in a regulated hot air oven (regulation better than ± 0.1 °C). The temperature variation of the volume of the pycnometer was also taken into account.

The temperature dependences of the specific volume, the adiabatic compressibility (β_{ad}) and the Rao number (R_n) are shown in Figs. 1, 2 and 3 respectively. Utilizing our ultrasonic velocity data[8] on these substances, β_{ad}, R_n and the van der Waals' constant (b) have been calculated from the relations[15]

$$\beta_{ad} = v/V^2 , \quad R_n = M\, v\, (V)^{1/3}$$

and

$$b = M\, v \left[1 - \frac{R\,T}{M\,V^2} \left\{ \sqrt{1 + \frac{M\,V^2}{3\,R\,T}} - 1 \right\} \right]$$

where v, V and M are the specific volume, ultrasonic velocity and molecular weight respectively. R is the gas constant and T is the absolute temperature. Table 1 presents the values of b, $(1/V) \cdot (\mathrm{d}V/\mathrm{d}T)$ and $(1/v) \cdot (\mathrm{d}v/\mathrm{d}T)$ for the nematic and isotropic phases of HBT and OBT.

The specific volume increases linearly with temperature up to ~1 °C below the nematic-isotropic transition, and again so in the isotropic region. A small but sudden discontinuity is observed which clearly indicates that the transition is of first order. The sudden increase of the specific volume with temperature near the nematic-isotropic transition is attributed to a sudden change from the ordered nematic to the disordered and less densely packed liquid state. From the Table 1 it can be observed that the thermal expansion coefficient $[(1/v) \cdot (\mathrm{d}v/\mathrm{d}t)]$ is larger for the nematic than for the isotropic phase. This indicates that the increase of order with decreasing temperature is larger in the nematic than in isotropic phase.

The breadths of the nematic-isotropic transitions are ~1.6 °C and ~1.0 °C in HBT and OBT respectively. The nematic-isotropic transition in our case is less sharp than in cholesteryl myristate[16] and cholesteryl acetate[17] (within 0.5 °C), but it is much sharper than in p-azoxyphenetole[18] and cholesteryl nonanoate[19]. Applying Kopp's additivity rule[20], the contribution to the molar volume due to a single methylene group can be found from half the difference between the molar volumes of HBT and OBT. This comes out be be 16.89 cc/mole and 17.17 cc/mole in the nematic (70 °C) and isotropic (80 °C) phases respectively. These values are nearly equal to the contributions of the methylene group in the isotropic state of n-alkanes[21], alkylbenzenes[22] and alkylbiphenyls[23] (16.4, 16.6 and 17.1 cc/mole respectively), while they are substantially higher than in the solid state of n-alkanes[21] (i. e. 14.5 cc/mole). This clearly indicates that in the nematic

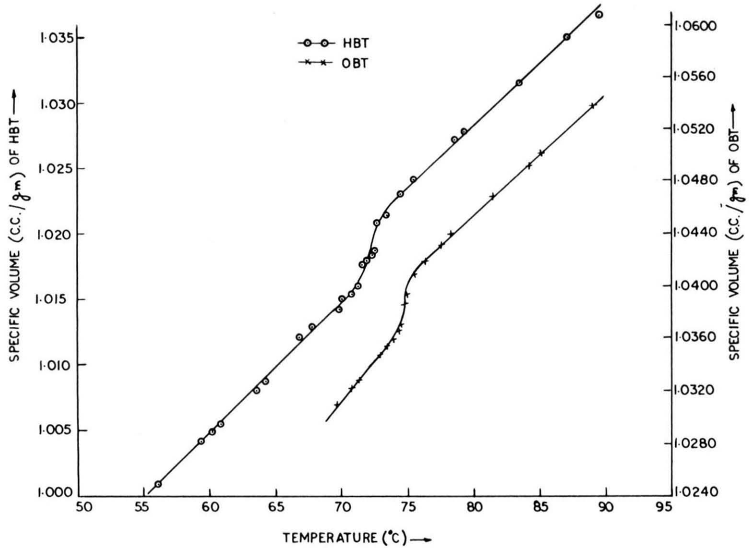


Fig. 1. Specific volume (c.c./gm) vs. temperature of HBT and OBT.

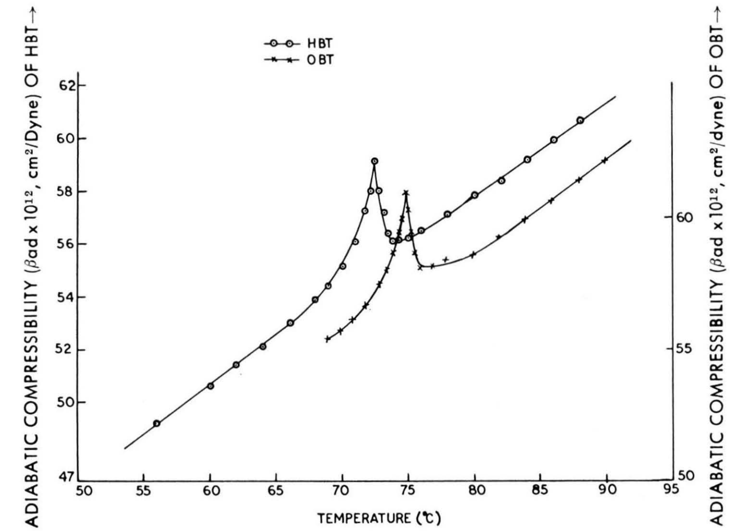


Fig. 2. Adiabatic compressibility (10^{-12} cm^2/dyne) vs. temperature of HBT and OBT.

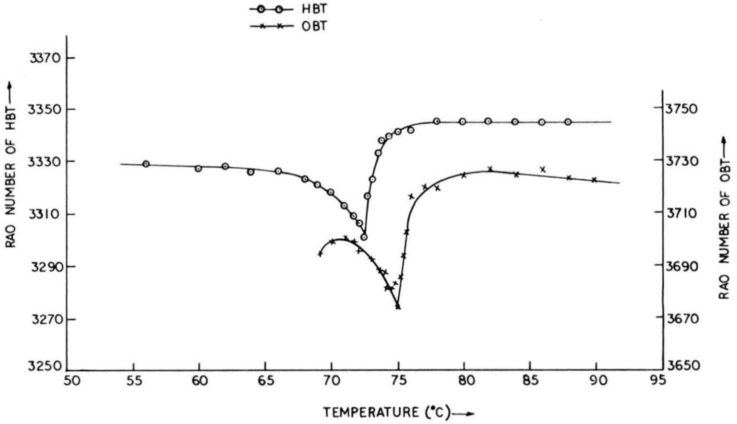


Fig. 3. Rao number [R_n in c.c. (meter/sec)$^{1/3}$] vs. temperature of HBT and OBT.

Table 1. Some parameters of HBT and OBT.

Sr. No.	Substance	Temperature and phase	b	$\frac{1}{v}\frac{dv}{dt}$ 10^{-4}/°C	$\frac{1}{V}\frac{dV}{dt}$ 10^{-3}/°C	$\frac{1}{V}\frac{dV}{dt} \Big/ \frac{1}{v}\frac{dv}{dt}$
1.	HBT	62 °C, nematic phase	286.84	9.79	3.16	3.22
		80 °C, isotropic phase	292.27	9.37	2.54	2.69
2.	OBT	72 °C, nematic phase	322.41	12.23	5.95	4.87
		84 °C, isotropic phase	327.34	8.97	2.43	2.71

phase the packing of the alkyl groups is closer to the isotropic than to the solid phase.

In HBT and OBT pretransitional variations in specific volume occur on the nematic side and are nearly absent on the isotropic side of the transition. This indicates that the pretransitional variations in HBT and OBT cannot be explained on the basis of Frenkel's heterophase fluctuation[24] theory, according to which they should occur on both sides of the transition. Our results accord with the Maier-Saupe theory[25, 26] which predicts the pretransitional variations to occur only on the nematic side of the transition. Nolle et al.[27] and Porter and Johnson[28, 29] believe that the pretransitional variations in specific volume occur on both sides of the transition. Recent investigations of Price and Wendorff[16, 17, 6]$_9$, however, are in accordance with our findings.

With the help of our experimental values of the specific volume jump $\Delta v_k / v_{nk} = 0.39\%$ for HBT and 0.36% for OBT and the values of

$$S_k \quad \text{and} \quad \frac{A}{k\, T_k\, V_{nk}^2} \ \text{vs} \ \frac{\Delta v_k}{v_{nk}}$$

listed in Maier-Saupe table[26], we obtained the degree of order (S_k) at the nematic-isotropic transition temperature to be 0.445 and 0.444 for HBT and OBT respectively. The value of A (the characteristic constant of the substance) is found to be 19.8×10^{-9} and 24.8×10^{-9} erg cm^6 for HBT and OBT respectively.

β_{ad} and R_n show pretransitional effects on both sides of the transition due to the pretransitional variation of the ultrasonic velocity on both sides of the transition and hence can be explained on the basis of Frenkel's heterophase fluctuation theory[8, 11]. The contribution of the CH_2 unit to the Rao number in these Schiff's bases turns out to be 190.3 in the nematic phase (70 °C) and 189.2 in the isotropic phase (80 °C). These values tally well with those of olephenes[15]. From Table 1 it is seen that the ratio of the coefficients of ultrasonic velocity $[(1/V) \cdot (dV/dt)]$ and thermal expansion $[(1/v) \cdot (dv/dt)]$ is nearly equal to 3 for HBT, which is in accordance with Rao's observation for unassociated liquids[30, 31]. For OBT, however, this ratio differs significantly from 3 on the nematic side (4.87 at 72 °C) while it is nearly equal to 3 on the isotropic side too (i. e. 2.71 at 80 °C).

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