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Specific Volume Studies in Nematic, Smectic–A and Smectic–C Phases of TBBA

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The specific volume, v, of Terephthalylidene-bis-*p*-*n*-butylaniline (TBBA) is measured as a function of temperature from the nematic phase to the smectic C phase. The compound exhibits nematic, smectic A, smectic C, smectic G and smectic H phases. The changes in specific volume across the nematic to smectic A and smectic A to smectic C phase transformations and the calculated thermal expansion coefficients confirm the order of the N–S_A transition as first order and S_A–S_C transition as second order. The volume jump across the N–S_A transition is 0.16%.

INTRODUCTION

The nematic to smectic A phase transition in liquid crystals has gained considerable interest after the McMillan,[1] Kobayashi[2] and de Gennes[3] theories and experimental results.[4,5] This transition is virtually first order in some compounds which are weakly polar,[6] while it is second order,[7] in other compounds exhibiting strong polar nature. In general the associated change in the order parameter at this transition is small while the reflected changes in the volume, ultrasonic velocity, optical textures, extra ordinary refractive index etc., are significant. Considerable work on TBBA (Terephthalylidene bis-*p*-*n*-butylaniline) has been already reported by others[8] and the present paper reports the volumetric measurements in the smectic–C, smectic A and nematic phases of TBBA.

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EXPERIMENTAL

The Specific Volume measurements were performed with a bicapillary pycnometer[6] containing a sample of approximately 4 ml. The diameter of the capillary is about 0.35 mm and the accuracy in specific volume is $\pm 0.1\ \mathrm{m}^3 \cdot \mathrm{kg}^{-1}\ 10^{-6}$. The permitted temperature control is ±0.1°C for a length of time ranging from 0.5 to 3 hr. The maximum permitted heating or cooling rate is 4°C/hr. The cooling rate in the present experiment is 2°C/hr.

The sample was prepared by condensation of *p*-*n*-butylaniline (0.2 mole) and terephthaldehyde (0.1 mole) in refluxing ethanol in the presence of a few drops of acetic acid. After refluxing the reactants for four hours, the solvent was removed by distillation. The crude TBBA was several times recrystallized from absolute ethanol until the observed transition temperatures were constant. The sample was pale yellow or gold coloured amorphous powder in its solid state and turned to yellow even after one heating. The transition temperatures were determined using a polarising microscope. Special precautions were taken to keep the sample away from atmospheric hydrolysis since the sample has shown a tendency to decompose. The decomposition was indicated by a change in colour, transition temperatures, widening in transition temperature range and specific volume values. The transition temperatures in °C are as follows:

$$\begin{tikzcd}
\mathrm{Solid} \arrow[r, "113"] & S_G \arrow[r, leftrightarrow, "144.0"] \arrow[d, bend left] & S_C \arrow[r, leftrightarrow, "170.5"] & S_A \arrow[r, leftrightarrow, "199.2"] & N \arrow[r, leftrightarrow, "235.4"] & I \\
S_{VI} \arrow[u] & S_H \arrow[l, "74"'] & & & &
\end{tikzcd}$$

RESULTS AND DISCUSSIONS

Specific volume variation with temperature is illustrated in Figure 1. The thermal expansion coefficient, α, variation with temperature is shown in Figure 2. The thermal expansion coefficient is calculated from the relation $\alpha = (1/V_n)(\Delta V/\Delta T)$ where V_n is the average molar volume for the temperature difference of ΔT and ΔV is the molar volume across the temperature of ΔT.

The compound exhibits high temperature nematic phase followed by smectic A, smectic C, smectic G and smectic H phases. Previously Guillon and Skoulios reported[8] variation of the molar volume and thickness of the smectic layers as a function of temperature in smectic

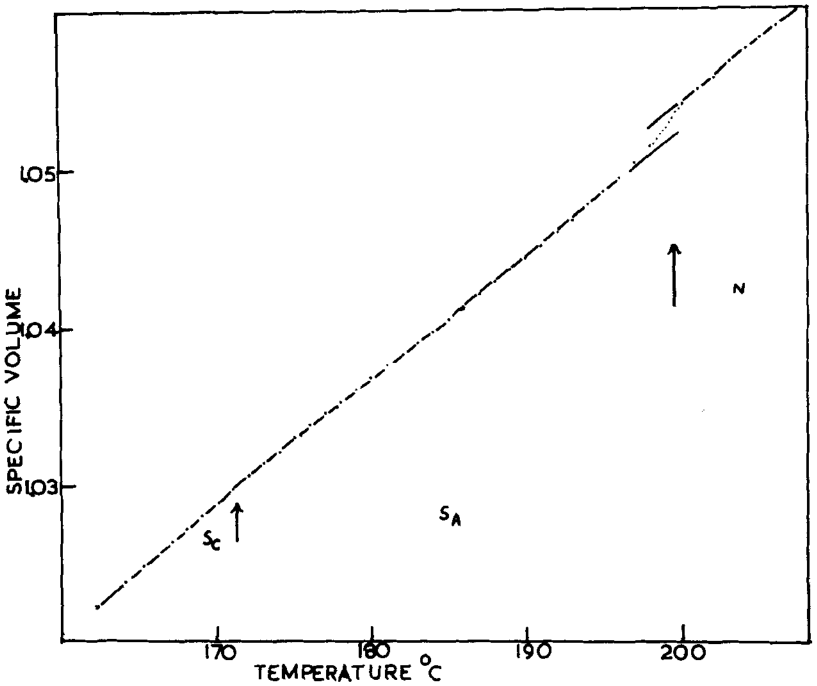

FIGURE 1 Variation of specific volume, v in (m^3 kg 10^{-3}) with temperature in nematic, smectic A and smectic C phases in TBBA.

G (formerly reported[12] as smectic B), smectic C and smectic A phases. The smectic A to nematic transition was not studied in TBBA and since this transition is involved in controversy, we have carried out the specific volume studies in nematic and smectic A phases in addition to smectic C phase.

The McMillan theory predict a first order transition i.e., the (T_{NA}/T_{NI}) value is 0.93 for TBBA. TBBA is weakly polar and exhibits monolayer molecular arrangement in its smectic A phase. The molecular length as measured by model is 28.6 Å while the layer thickness in the smectic A phase is 28.3 Å.[9] Large pretransitional effects with small latent heat are already reported.[10] The reported transition enthalpy associated with the N–S_A transition is 0.14 K.Cal/mol,[11] (0.16 K.Cal/mol;[12] 0.07 K.Cal/mol[10]) at this transition. Bhattacharya *et al.*[13] also confirmed the first order N–S_A transition in this compound. They observed an anomalous decrease in ultrasonic velocity and a peak in attenuation at this transition.

The volume jump across this transition is ($\Delta V/V$) = 0.16% and the thermal expansion coefficient suggests a first order phase transition.

The N–S_A transition is independent from the interference of other N–I and S_A–S_C transitions. The compound exhibits a wide range of nematic phase ≈ 35 °C preceded by a wide range of smectic A phase ≈ 28 °C in the heating cycle thereby accounting non-interference of the other transitions, i.e., N–I and S_A–S_C phase transitions.

The salient features of the N–S_A transition are as follows.

1) At the nematic–smectic–A transition the pale yellow opaque appearance of the nematic phase is transformed into the translucent appearance of the smectic phase.

2) The thermal expansion coefficient shows a maximum at the phase transition. However the value of the thermal expansion coefficient is almost same in both smectic A and nematic phases.

3) The slope value in the smectic A phase is slightly smaller than the slope value in the nematic phase. The pre-transitional effects are found to occur on both sides of the transition. We have also observed the co-existence of a two phase region for about 1.4 °C. From 199.4 °C to 198.0 °C the compound in the bulb did not appear to be homogeneous but rather as a two phase mixture. The opaque nematic phase

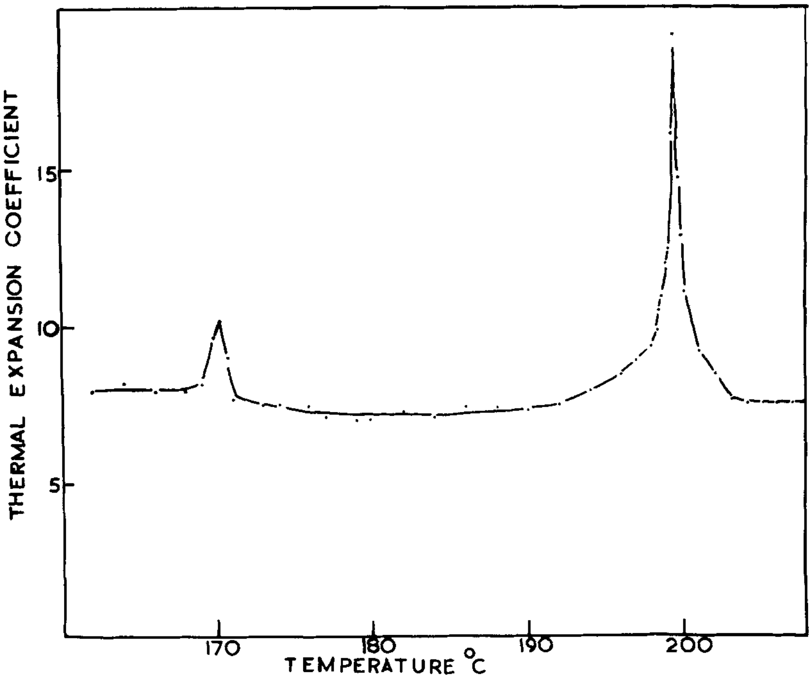

FIGURE 2 Variation of thermal expansion coefficient, α in (10^{-4} °C^{-1}) with temperature in TBBA.

floated above the slowly developing translucent smectic A phase and the separation of these two phases was identified visually. However the rate of cooling has a small effect i.e., ±0.2°C on the existence of two phase phenomena.

An estimate of the pressure dependence of the nematic to smectic-A transition temperature can be given using the clausius-clapeyron equation

$$\frac{dT_t}{dP} = T_t \cdot [\Delta V/\Delta H]$$

where T_t is the transition temperature, P is the pressure, ΔV is the volume change associated with the transition and ΔH is the heat of transition. The $[(dT_t/dP) = 50.41$ K/k.bar)] value at the S_A–N transition for TBBA is higher than the results for PAA and other nematic-isotropic transitions. It can be explained that this high value is probably due to the variance of ΔH values[10-12] for TBBA. For a pure sample ΔH value must be high so that lower (dT_t/dP) value will be obtained.

We also measured the specific volume variation with temperature from smectic A into the smectic C phase and do not observe the volume jump at the S_A–S_C transition. However a continuous change in volume and a change in slope observed at this transition suggest a second order S_A–S_C transition and is in agreement with other reported results.[8,14] A small kink is found in thermal expansion coefficient which suggests a very weak first order or a second order transition. Such a type of behaviour is expected at this transition in TBBA because of non-interference of other phase transformations with this S_A–S_C transition.

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