Ultrasonic Studies in N-(p-n-butoxybenzylidene)-p-n-butylaniline

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The ultrasonic velocity in the $S_0(S_1)$, $S_B$, $S_A$, $N_B$, $N_0$ and isotropic liquid phases of N-(p-n-butoxybenzylidene)-p-n-butylaniline (BBBA) has been measured as a function of temperature. A transition in the nematic phase seems to indicate the existence of an ordinary nematic and a cytacticotropic phase. The transition $S_B$-$S_A$ has been found for the first time with the ultrasonic velocity method. The adiabatic compressibility $\beta_{ad}$ and the molar sound velocity $R_n$ (Rao number) have been determined using the experimental density and ultrasonic velocity.

Introduction

The interest in liquid crystals has greatly increased during the last two decades because of important application [1, 2]. The ultrasonic properties of liquid crystals provide additional information about the different phases and phase transitions in these compounds. It is well known that the liquid crystals often exhibit polymorphism [3, 4]. Though ultrasonic experiments on liquid crystals were reported [5] as early as 1955, the amount of information obtained so far is comparatively meagre and referred to only in the review articles by Natale [3] and Candau and Letcher [4]. The phase changes with temperature which appear in ultrasonic experiments usually confirm the results of other experiments like X-ray studies, thermal microscopy, Differential scanning calorimetry etc.

The liquid crystal phases of the Schiff base homologous series N-(p-n-alkoxy benzylidene) p-n-alkylanilines are usually complicated and require a careful investigation of their physical properties. The general structural formula of the series is given in Figure 1.

$$C_nH_{2m+1}O\bigg\langle\bigg\langleCH=N\bigg\rangle\bigg\rangle\bigg\rangle_{C_m}H_{2m+1}$$

Fig. 1.

The notation follows no. m [6, 7], where n indicates the alkoxy carbon number and m indicates the alkyl carbon number.

Ultrasonic velocity measurements in liquid crystals of the no. m series were reported by several authors [8, 9, 10, 11]. The ultrasonic velocity variation with temperature was reported at the smectic-nematic transition in OBT [9] and at the smectic-nematic and smectic-smectic transitions in NBT [11]. The authors are not aware of ultrasonic velocity measurements in mesophase compounds exhibiting four or more phases.

The present study was carried out on the 40.4 compound, namely N-(p-n-butoxybenzylidene)-p-n-butylaniline (BBBA). The phase transitions found are consistent with our previous density [12] and thermal microscopy [13] studies. The sequence of the phase transitions is given below.

$$C_8H_{17}O\bigg\langle\bigg\langleCH=N\bigg\rangle\bigg\rangle_{C_4}H_9$$

Solid $\rightarrow S_G \rightarrow S_B \rightarrow S_A \rightarrow N_B \rightarrow N_0 \rightarrow I$

Fig. 2.

Experimental

The synthesis of the compound is described elsewhere [12]. The compound exhibits mesophase-mesophase and mesophase-isotropic transitions at temperatures which are accurate to within 0.1 °C in heating and cooling cycles as well.

The ultrasonic velocity was measured at a frequency of 2 MHz using the ultrasonic interferometer U1901 NPL, INDIA. The cell was essentially that supplied with the interferometer except for a few modifications for the heating arrangement. The temperature of the cell was controlled by the current flowing through the heating element surrounding the cell. The ultrasonic velocity measurements are accurate to 0.2%.

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Results

The ultrasonic velocity ($V$) was investigated in the temperature range of 38 °C—82 °C with special attention in the neighbourhood of the transition temperatures. Specific volume ($v$), adiabatic compressibility ($\beta_{ad}$), and molar sound velocity ($R_n$) or Rao Number were evaluated from the experimental results using the equations

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

where $\rho$ is the density and $M$ is the molecular weight.

The ultrasonic velocity variation with temperature is shown in Figure 3. The region of the transitions N$_C$-S$_A$ and S$_A$-S$_B$ is shown in greater detail in the inset 3a. Figures 4, 5 and 6 show the variation of the derived parameters $\beta_{ad}$ and $R_n$ with temperature.

Discussion

Figure 3 indicates a sharp decrease in ultrasonic velocity across the isotropic-nematic transition. In the isotropic and nematic phases the ultrasonic velocity increases linearly with decrease of temperature. However one can observe an anomalous behaviour at the transition temperatures (a sharp decrease in $V$). It is well established that the ultrasonic velocity is related to the molecular structure and the nature of intermolecular interactions [14]. The observed increase in $V$ with decreasing temperature in the isotropic phase may be attributed to the decrease in the intermolecular distance and consequent increase in the potential energy of interaction. The sharp decrease of $V$ in the isotropic liquid-nematic transition can be attributed to an increase in molecular order.

Figures 4 and 5 reveal that the adiabatic compressibility decreases linearly with decreasing temperature, unlike the ultrasonic velocity. A sudden jump is noticed in the $\beta_{ad}$ vs. temperature graph at the isotropic-nematic transition. The variation of $\beta_{ad}$ and $R_n$ reflects pretransitional effects in the ultrasonic velocity which can be explained on the basis of Frenkel's heterophase fluctuation theory [15].

Several authors reported a nematic phase up to 46 °C in this compound. According to them the nematic phase extends from 74 °C to 46 °C. However from our ultrasonic velocity and density [12] measurements we could observe a phase transition at 59.4 °C. To further check this transition temperature we made a preliminary study on the dielectric constant variation with temperature and
could confirm this phase transition at 59.4 °C. It may be pointed out that this transition is reported for the first time. We believe from our density, ultrasonic velocity, thermal microscopy and dielectric constant studies that this transition might be from ordinary nematic to cybotactic nematic. We have yet to confirm this new phase by X-ray and other techniques.

The changes in velocity at Nc-SA and SA-SB are marked by a change in slope in the velocity vs. temperature graph, Figure 3. At the SB-SG transition a broad dip is observed due to the transformation from the two dimensional SB to the three dimensional SG phase [7].

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