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

J. V. Rao and C. R. K. Murty
Physics Department, Nagarjuna University, Nagarjuna Nagar, India

Z. Naturforsch. **36a**, 1002—1005 (1981); received June, 11 1981

The ultrasonic velocity in the $S_G(S_H)$, S_B, S_A, N_c, 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 cybotactic nematic phase. The transition S_G-S_B has been found for the first time with the ultrasonic velocity method. The adiabatic compressibility β_{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.

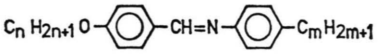
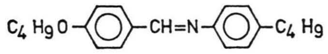


Fig. 1.

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.



$$\text{Solid} \xleftrightarrow{12\,^\circ C} S_G \xleftrightarrow{40.5\,^\circ C} S_B \xleftrightarrow{44.4\,^\circ C} S_A \xleftrightarrow{45.3\,^\circ C} N_C \xleftrightarrow{59.4\,^\circ C} N_O \xleftrightarrow{74\,^\circ C} I$$

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 UI601NPL, 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%.

Reprint requests to Prof. C. R. K. Murty, Physics Department, Nagarjuna University, Nagarjuna Nagar 522510, Indien.

0340-4811 / 81 / 0900-1002 $ 01.00/0. — Please order a reprint rather than making your own copy.

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 (β_{ad}), and molar sound velocity (R_{n}) or Rao Number were evaluated from the experimental results using the equations

$$v = 1/\varrho\,, \quad \beta_{\mathrm{ad}} = v/v^2, \quad R_{\mathrm{n}} = M\,v\,(V)^{1/3},$$

where ϱ 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 $\mathrm{N_C}$-$\mathrm{S_A}$ and $\mathrm{S_A}$-$\mathrm{S_B}$ is shown in greater detail in the inset 3a. Figures 4, 5 and 6 show the variation of the derived parameters β_{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 β_{ad} vs. temperature graph at the isotropic-nematic transition. The variation of β_{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 upto 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

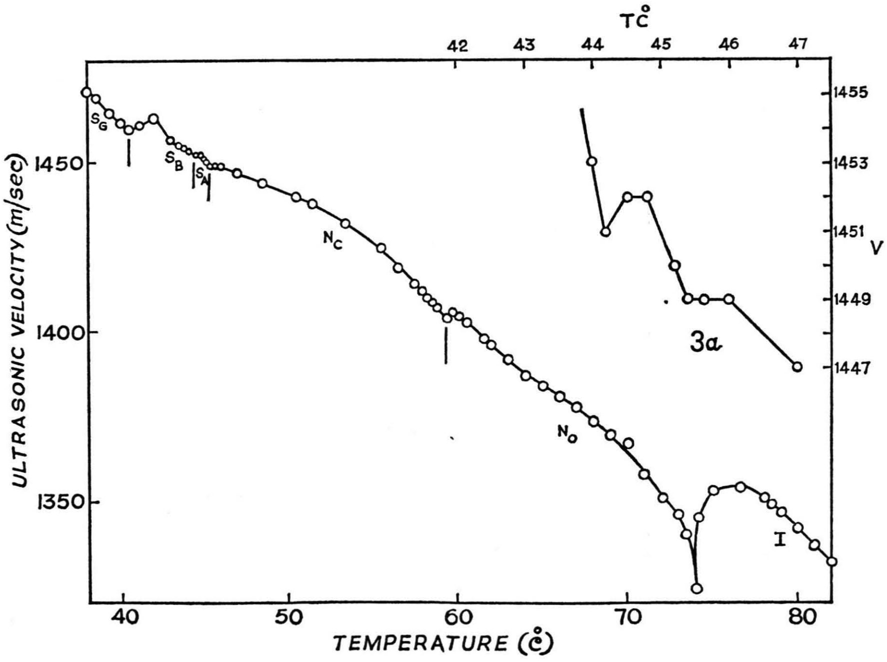


Fig. 3.

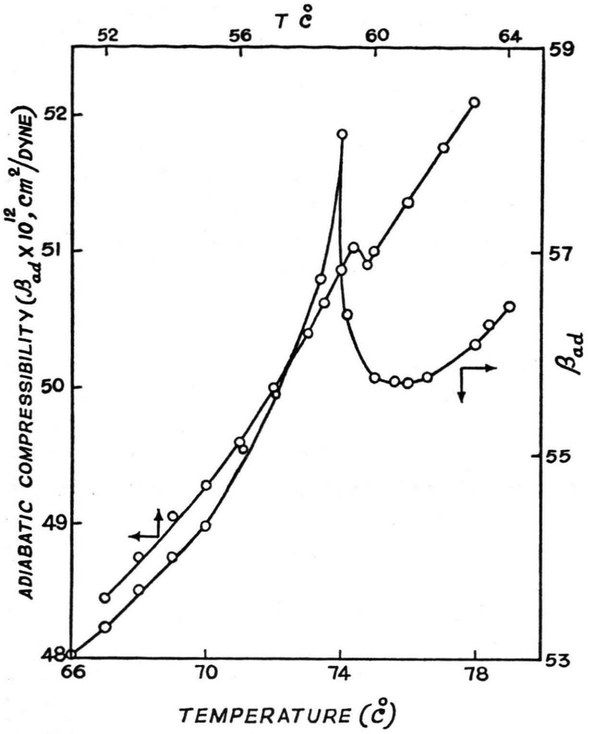


Fig. 4.

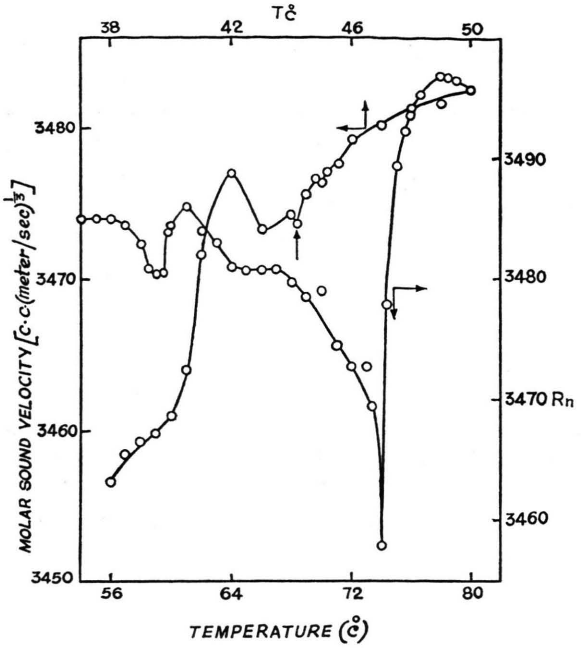


Fig. 6.

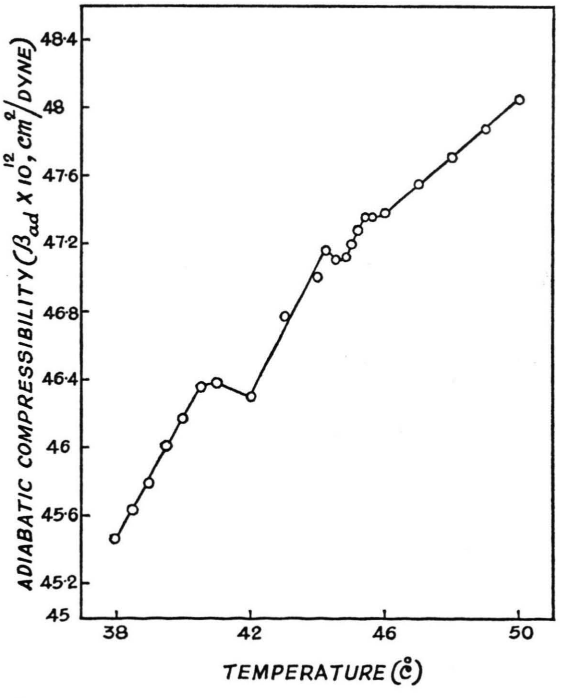


Fig. 5.

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 N_C-S_A and S_A-S_B are marked by a change in slope in the velocity vs. temperature graph, Figure 3. At the S_B-S_G transition a broad dip is observed due to the transformation from the two dimensional S_B to the three dimensional S_G phase [7].

Acknowledgements

The authors thank Dr. N. V. S. Rao and Dr. V. G. K. M. Pisipati for their valuable suggestions, Prof. Dr. K. V. J. Rao, Department of Chemistry for his help in the synthesis and purification of the sample and CSIR and Electronics Commission, New Delhi for financial assistance.

[1] L. A. Goodman, R. C. A. Rev. **35**, 613 (1974).

[2] Liquid Crystal Display, Elector **61**, 34 (1980).

[3] G. G. Natale, J. Acoust. Soc. Amer. **63**, 1265 (1978). ibid. **65**, 1677 (1978).

[4] S. Candau and S. V. Letcher, Advances in Liquid Crystals Vol. 3, Academic Press Inc., New York 1978.

[5] I. Gabrielli and L. Verdini, Nuovo Cim. **2**, 426 (1955).

[6] G. W. Smith and Z. G. Gardlund, J. Chem. Phys. **59**, 3214 (1973).

[7] A. J. Leadbetter, M. A. Mazid, B. A. Kelly, J. W. Goodby, and G. W. Gray, Phys. Rev. Lett. **43**, 630 (1979).

[8] J. R. Otia and A. R. K. L. Padmini, Ind. J. Pure Appl. Phys. **11**, 190 (1973).

[9] B. Bahdur, Acustica **33**, 277 (1975).

[10] B. Bahadur, J. Phys. C. Sol. State Phys. **9**, 11 (1976).

[11] A. P. Kapustin and G. E. Zevera, Soc. Phys. crystallogr. **10**, 603 (1966).

[12] J. V. Rao, N. V. S. Rao, V. G. K. M. Pisipati, and C. R. K. Murty, Ber. Bunsenges. Phys. Chem. **84**, 1157 (1980).

[13] J. V. Rao, N. V. S. Rao, V. G. K. M. Pisipati, and C. R. K. Murty, Mol. Cryst. Liq., Cryst. Lett. (Communicated).

[14] R. R. Beyer and S. V. Letcher, Physics Ultrasonic New York Academic Press, New York 1969.

[15] J. Frenkel, Kinetic theory of liquids, Bover, New York 1975.