Phase Transition Studies in PMBAB and PEBAB

V. G. K. M. Pisipati * and N. V. S. Rao **
Faculty of Physical Sciences, Nagarjuna University, Nagarjunanagar 522 510, India

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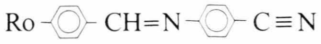
The variation of density and ultrasonic velocity with temperature in N-(p-methoxybenzylidene)-p-aminobenzonitrile (PMBAB) and N-(p-ethoxybenzylidene)-p-aminobenzonitrile (PEBAB) are presented. The density jumps and thermal expansion coefficients suggest the nematic-isotropic transition of both compounds to be of first order. The adiabatic compressibility β_{ad}, molar sound velocity R_n and molar compressibility A_w are computed. The contribution of a methylene unit to the molar volume is found to be higher than literature values. The anomalous ultrasonic velocity dip at the nematic-isotropic transition for both compounds is found to be high; the value is many times those found for other nematic-isotropic or nematic-smectic A transitions.

Introduction

A system of long molecules without any attractive interaction can undergo a first order phase transition from the isotropic to the anisotropic phase as the molar volume is decreased with decreasing temperature [1]. A study of the temperature dependence of physical properties such as molar volume [2], ultrasonic velocity [3] and derived parameters such as adiabatic compressibility, molar sound velocity or Rao number [4] and molar compressibility or Wada constant [5] gives information regarding the nature of the phase transition and pretransitional effects in the vicinity of the phase transformation. Cyano-substituted liquid crystals have numerous applications because of the specific importance of their singular characteristics, e.g., ready response to electric fields (TN cells), induction of reentrant smectic A nematic phases etc. In view of their importance we carried out measurements of the temperature dependence of the density and ultrasonic velocity of two cyano-compounds: N-(p-methoxybenzylidene)-p-aminobenzonitrile (PMBAB) and its higher homologue N-(p-ethoxybenzylidene)-p-aminobenzonitrile (PEBAB), involving the nematic and isotropic phases.

Experimental

The compounds were prepared by condensation of the p-n-alkoxybenzaldehyde (0.1 mole) and p-aminobenzonitrile (0.1 mole) in refluxing absolute ethanol in the presence of a few drops of glacial acetic acid to give the crude N-(p-alkoxybenzylidene)-p-aminobenzonitrile. After refluxing the reactants for four hours, the solvent was removed by distillation under reduced pressure. The crude compounds were recrystallized several times from absolute ethanol to give the pure gold-coloured crystalline compounds. Crystallization was continued until the transition temperatures were found to be constant. The density was measured using a bicapillary pyknometer. The absolute error in density was $\pm 0.1\ \mathrm{kg \cdot m^{-3}}$. The permitted temperature control was ±0.1 °C for a length of time ranging from half an hour to three hours. The maximum permitted heating or cooling rate was 4 °C per hour. The cooling rate in the present experiments was 1 °C per hour. The ultrasonic velocity was measured with a modified 2 MHz ultrasonic interferometer (model UF 101 NPL India). The temperature control was ±0.1 °C and the accuracy in the ultrasonic velocity was $\pm 0.4\ \mathrm{m \cdot s^{-1}}$. The observed transition temperatures are presented below.



$$R = C_2H_5 \text{ Crystal } \xrightleftharpoons{105\,°C\ (105\,°C)}$$

$$\text{Nematic } \xrightleftharpoons{125.5\,°C\ (124.5\,°C)} \text{ Isotropic PEBAB}$$

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* Department of Physics.
** Department of Chemistry.

Reprint requests to Dr. N. V. S. Rao, Faculty of Physical Sciences, Department of Chemistry, Nagarjuna University, Nagarjunanagar 522 510, Indien.

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$$R = CH_3 \quad \text{Crystal} \xrightleftharpoons{106\,°C\ (103\,°C)} \text{Nematic} \xrightleftharpoons{118\,°C\ (113.5\,°C)} \text{Isotropic PMBAB.}$$

The literature values (in brackets) are taken from [13].

Results and Discussion

The temperature dependence of the density and ultrasonic velocity are illustrated in Figs. 1 and 2, respectively. The thermal expansion coefficient $\alpha = d\ln V/dT$ of PMBAB and PEBAB at different temperatures is illustrated in Fig. 3 (V = average molar volume, for the temperature difference ΔT, and ΔV is the molar volume change for the temperature change ΔT). The adiabatic compressibility β_{ad}, molar sound velocity R_n, and molar compressibility A_w are calculated from the following relations

$$\beta_{ad} = v/V_u^2\,; \quad R_n = M_v V_u^{1/3}\,; \quad A_w = M_v \cdot \beta_{ad}^{-1/7}\,;$$

where v is the specific volume, M_v = molar volume and V_u = ultrasonic velocity.

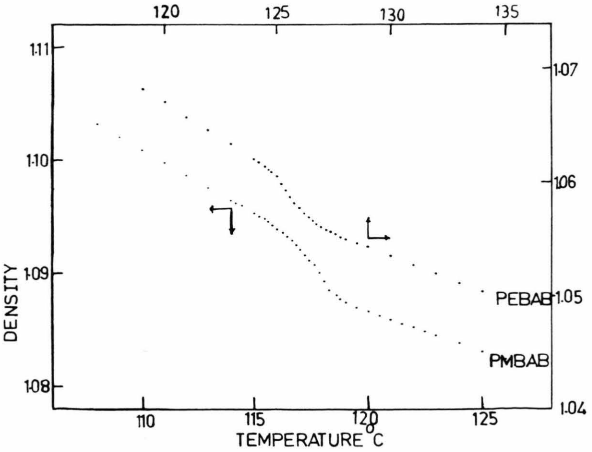

Fig. 1. Variation of the density (in 10^3 kg m^{-3}) with temperature in the isotropic and nematic phases of PMBAB, PEBAB.

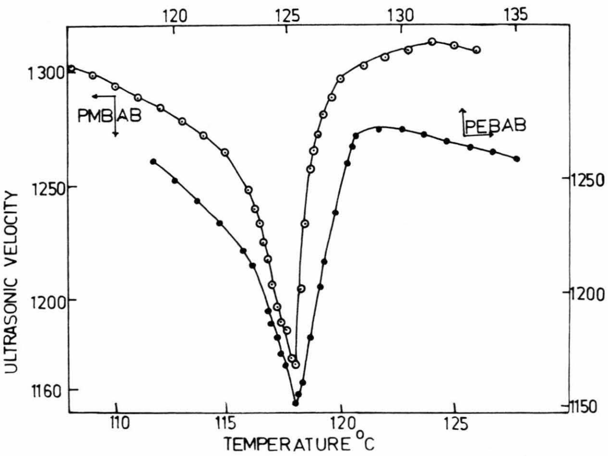

Fig. 2. Variation of the ultrasonic velocity (in m s^{-1}) with temperature in the isotropic and nematic phases of PMBAB and PEBAB.

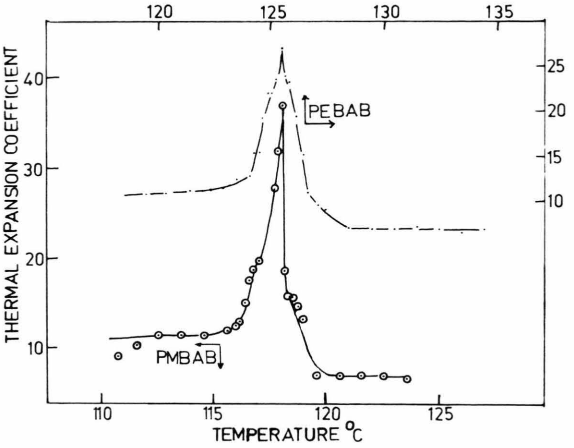

Fig. 3. Variation of the thermal expansion coefficient α (in °C^{-1} 10^{-4}) with temperature for PMBAB and PEBAB.

The density of both PMBAB and PEBAB increases linearly with decreasing temperature in the isotropic and nematic phases with a sudden increase at the isotropic-nematic transition. The molar volumes of PMBAB and PEBAB in the isotropic liquid phase at $(T_{NI} + 5)$ °C are 217.85 and 237.65 10^{-6} m^3, respectively. If additivity of the molar volumes is assumed, the increment per methylene group estimated from the difference in molar volumes of the two compounds in the isotropic phase is 19.8 10^{-6} m^3 and is by ≈ 14% higher than the value observed for other homologous series, e.g., N-(p-n-alkoxybenzylidene)-p-n-alkylanilines [6, 7] and alkylbenzenes [8]. Also the contribution of a CH_2 unit (19.2 10^{-6} m^3) in the nematic phase is smaller than in the isotropic phase, and this indicates closer packing in the nematic phase than in the isotropic phase. The discontinuities in density and the peaks in the thermal expansion coefficient at the transition temperatures

Table 1. Density changes at the transition temperature, and calculated and theoretical values of molar sound velocity and molar compressibility.

Compound	$\Delta\varrho/\varrho$ % at T_{NI}	Isotropic phase			
		Molar sound velocity		Molar compressibility	
		Experimental	Theoretical	Experimental	Theoretical
PMBAB	0.37	2387	2399	123.5	121.1
PEBAB	0.29	2587	2594	132.8	130.2

indicate first order phase transitions. The observed densit jumps (Table 1) for PMBAB and PEBAB are found to be in accordance with literature data [2, 9, 10] for NI transitions.

The ultrasonic velocity increases linearly with decreasing temperature (Fig. 2) in the isotropic phase up to the transition temperature, following the normal behaviour of liquids. This increase in velocity is explained in terms of the decrease in mean distance between the molecules thereby increasing the potential energy of interaction between the molecules. The velocity reaches a minimum at the transition temperatures, increases sharply below the transition and then shows a linear increase on the lower temperature side for the nematic phase. This increase for PMBAB (11.4%) and PEBAB (10%) at the N−I transformation is anomalously sharp compared with the normal behaviour of the linear temperature dependence of V_u, and these values are also many times greater than those found for other N−I [11] or N−S_A transitions [12]. The ranges of anomalous behaviour are 3 °C and 2.8 °C for PMBAB and PEBAB, respectively. The sharp decrease in the vicinity of the isotropic-nematic transformation is due to the transformation of the disordered isotropic liquid phase to the nematic phase with its associated long range orientational order of the molecules.

Our study of the variation of α with temperature indicates that a) α versus T attains a maxima at the transition temperatures $T_{NI} = 118$ °C for PMBAB and 125.5 °C for PEBAB, indicating a first order transition; b) α versus T shows a symmetric variation on either side of the transition. The higher value of α for the nematic phase compared with that for the isotropic phase again indicates higher ordering of the molecules in the nematic phase than in the isotropic phase.

The variation of adiabatic compressibility β_{ad} (Fig. 4) with temperature suggests pretransitional effects on both sides of the transition. The pretransitional effects in the isotropic phase of PMBAB are predominant over those in PEBAB. The pretransitional effects in the isotropic liquid can be attributed to the small heat of transition from the nematic phase to the isotropic liquid.

The molar sound velocity R_n and molar compressibility A_w show an interesting variation with

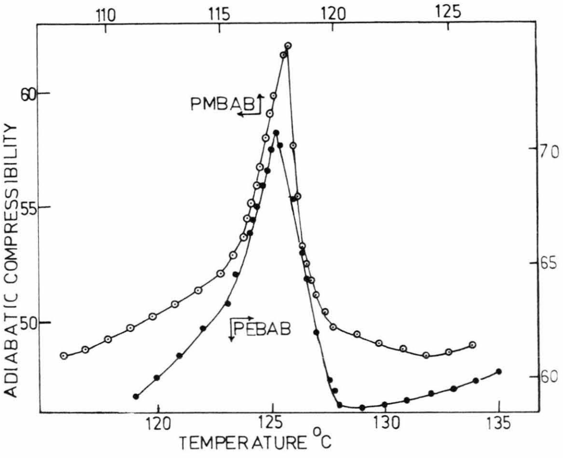

Fig. 4. Variation of the adiabatic compressibility $\beta_{ad} \times 10^{-3}$ m kg^{-1} s^2 with temperature for PMBAB and PEBAB.

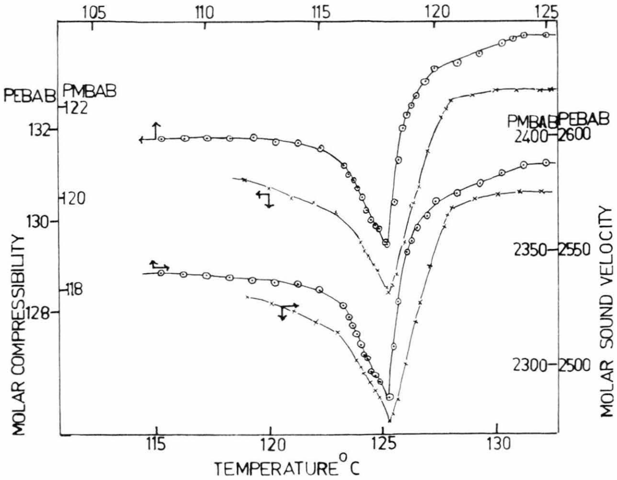

Fig. 5. Variation of the molar sound velocity, $R_n \times 10^{-6}$ m$^{10/3}$ s$^{-1/3}$ and molar compressibility $A \times 10^{-31/7}$ · m$^{20/7}$ kg$^{1/7}$ s$^{-2/7}$ with temperature for PMBAB and PEBAB. ×: PEBAB; ○ PMBAB.

temperature (Figure 5). Far from the T_{NI} transition, R_n and A_w are found to be constant in the isotropic and nematic phase. However, they suddenly fall above T_{NI} and then gradually increase below T_{NI} with decreasing temperature. The ΔR_n and ΔA_w are found to be 188×10^{-6} m$^{10/3}$ s$^{1/3}$ and 9.3×10^{-31} m$^{20/7}$ kg$^{1/7}$ s$^{-2/7}$, respectively, for a methylene unit contribution. The results are in good agreement with literature data [7] for the isotropic phases of compounds exhibiting mesophases. The values of R_n and A_w calculated from the experimental density and ultrasonic velocity are in good agreement with theoretical data (Table 1). The values of $[(\mathrm{d}\ln V_u/\mathrm{d}T)/(\mathrm{d}\ln v/\mathrm{d}T)]$ are 2.51 and 2.82 for PMBAB and PEBAB in the isotropic region and are close to Rao's value (= 3) for unassociated liquids [4]. In the isotropic region, the mean values of $(\mathrm{d}\ln \beta_{ad}/\mathrm{d}T)/(\mathrm{d}\ln v/\mathrm{d}T)$ for PMBAB and PEBAB are 5.98 and 6.9 respectively, in good agreement with the value of Wada [5] which is 6.5 for several organic liquids.

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