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# Characterization of Some Liquid Crystals through Sound and Thermodynamic Parameters

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# Characterization of Some Liquid Crystals through Sound and Thermodynamic Parameters

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*The structural changes arising from transition between the mesophases of liquid crystalline materials can be better understood by ultrasound in conjunction with specific volume properties. In particular, ultrasonic studies are found to give clear information regarding the nature of the phase transition, pretransitional effects, and molecular ordering. For example, temperature corresponding to the maximum value of acoustic impedance, adiabatic compressibility, and temperature corresponding to the minimum value of ultrasonic velocity, Rao's number, order parameter, and molar compressibility, in thermotropic liquid crystals are very useful in understanding their structural behavior. In view of these facts, it was thought worthwhile to study ultrasonic velocity with data available for density measurements on pure samples of nematics, namely, 4,4′-azoxy anisole and 4,4′-dibutoxy azoxy benzene. The results of this work, are presented in this article and discussed.*

**Keywords:** liquid crystals; mesophases; phase transition; sound velocity

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## INTRODUCTION

The study of propagation of ultrasonic waves in pure liquids, liquid crystalline materials, has attracted the attention of many workers in the recent past [1–27]. In particular, such a study in conjunction with density (or specific volume) determination has been found to be useful in drawing conclusions about intermolecular interactions, charge transfer complexations, structure of the molecules, and so forth. Also, these studies enable one to derive several thermodynamic and acoustical parameters and their excess values. The derived physical parameters, such as molar sound velocity or Rao's number ($R$), molar compressibility or Wada's constant (B), characteristic acoustic impedance ($Z$), intermolecular or free length ($L_f$), free volume ($V_f$), available volume ($V_a$), and adiabatic compressibility ($\beta$) play important roles in the phenomenon of sound transmission. For example, the parameter $Z$, which is determined by the product of density ($d$) and ultrasonic velocity ($c$), has a greater significance as a characteristic property of the medium than does either the density or velocity individually. Similarly, in sound transmission, the molar sound volume (Vm) is of more concern than molar sound velocity or Rao's number.

A search in the literature [4–14] indicates that the structural changes arising from transition between the mesophases of liquid crystalline materials can be better understood by ultrasound conjunction with specific volume properties. In particular, ultrasonic studies are found to give clear information regarding the nature of the phase transition, pre-transitional effects, and molecular ordering. For example, temperature corresponding to the maximum value of acoustic impedance, adiabatic compressibility, and temperature corresponding to the minimum value of ultrasonic velocity, Rao's number, order parameter, and molar compressibility, in thermotropic liquid crystals [15] and some of their mixtures are very useful in understanding their structural behavior. In view of these facts, we thought it worthwhile to study ultrasonic velocity with density measurements (available in literature [27]) on pure samples of nematics, namely, 4,4′-azoxy anisole and 4,4′-dibutoxy azoxy benzene, here after referred to as PAA and BOAB. The results of this work are presented and discussed.

## EXPERIMENTAL

The required data of the ultrasonic velocity ($C$) are obtained by measuring the wavelength in liquid medium by using an interferometer Type M81 with an accuracy of about $\pm 0.03$ m/s. The double-walled (provided for better insulation) measuring cell was provided with a

micrometer screw gauge of accuracy $\pm 0.0001$ cm. The sound velocities of some standard liquids such as benzene and cyclohexane were measured using this equipment and the results were compared. The comparison of these values shows that the measured wavelengths may be accurate to within 5 parts in 1,000 units. The heating arrangement is made with heating element placed over the measuring cell uniformly. Necessary insulation is made with mica sheets to avoid short circuiting. A calibrated thermocouple junction along with a temperature control unit was used to maintain the temperature to an accuracy of $\pm 0.1\,^{\circ}$C.



## DEFINING RELATIONS

For the derivation of several acoustical and thermodynamic parameters, the following defining relations reported in the literature are used:

Molar volume $(V_m) = M/d$.
Adiabatic compressibility $\beta = 1/(C^2 d)$.
Intermolecular free length $(L_f) = K\,(\beta)^{1/2}$ where $K$ is a temperature-independent constant given by 6.25 exp $-04$.
Available volume (Va: Schaffs) $= V_m\{1-(C/C_\infty)\}$ where $C_\infty = 1600\ \mathrm{ms}^{-1}$.
Available volume (Va: Kittel) $= \{V_m \cdot Cg \cdot 3^{1/2}/C\}$ where $Cg = \{\gamma\,(\text{ratio of specific heats}) \cdot RT/M\}^{1/2}$
Free volume $(V_f) = \{V_m \cdot (Cg \cdot /C)^3\}$.
Molar sound velocity or Rao's number (R) $= V_m \cdot (C)^{1/3}$.
Molar compressibility or Wada's number $= V_m \cdot (\beta)^{-1/7}$.
Thermal expansion coefficient $(\alpha) = (1/Vn)\ (\triangle V/\triangle T)$ where $Vn = \{(V_1 + V_2)/2\}$; $\triangle V = (V_2 – V_1)$; $\triangle T = (T_2 – T_1)$
Orientational order parameter (S: Maier Saupe) $= \{1 - 0.98\ (T/T_{N\text{-}I})\ (Vn/Vn_{N\text{-}I})^2\}^{0.22}$.
Orientational order parameter (S: Chandrasekhar) $= \{(1/2)\cos^2(2)^{1/2}\theta_{rms} + \cos(2)^{1/2}\theta_{rms}\}$ where $\theta_{rms}$ is given in terms of Einstein's characteristic temperature $\theta$. $\theta_{rms} = k'T(d^{2/3})_{\text{mean x}}\ x(C^2)_{mean}$ with $K' = 3.5256$ exp $-06$.
Characteristic acoustic impedance $Z = C \cdot d$ Rayls.

## RESULTS AND DISCUSSION

(Using the measured values of the ultrasonic velocity $C$ and the density $d$ (reported in an earlier work [27]), various physical parameters are derived with the help of their defining equations, listed above, and the results are presented in Tables 1 and 2. In particular,

**TABLE 1** The Variation of Specific Volume and Sound Velocity and Derived Quantities for PAA at Various Temp.

| $t$(°C) | $V$ (cc/gm) | $C$ m/s | $\beta \times 10^{12}$ cm$^2$/dyne | $R$ | $B$ | $A \times 10^4$ | S | $Z \times 10^{-6}$ rayls |
|---|---|---|---|---|---|---|---|---|
| 119 | 0.8441 | 1352.2 | 46.10 | 2411 | 6532 | 4.38 | 0.4667 | 1.60 |
| 120 | 0.8445 | 1351.1 | 46.26 | 2411 | 6533 | 17.98 | 0.4648 | 1.60 |
| 121 | 0.8460 | 1346.7 | 46.65 | 2413 | 6537 | 17.36 | 0.4629 | 1.59 |
| 122 | 0.8475 | 1346.7 | 46.73 | 2417 | 6546 | 14.97 | 0.4610 | 1.59 |
| 123 | 0.8487 | 1374.4 | 44.93 | 2437 | 6593 | 25.62 | 0.4591 | 1.62 |
| 124 | 0.8510 | 1324.4 | 48.51 | 2414 | 6538 | 14.33 | 0.4572 | 1.56 |
| 125 | 0.8522 | 1284.6 | 54.66 | 2370 | 6437 | 8.91 | 0.4553 | 1.51 |
| 126 | 0.8529 | 1320.0 | 48.95 | 2417 | 6545 | 9.38 | 0.4534 | 1.55 |
| 127 | 0.8537 | 1284.1 | 51.78 | 2397 | 6499 | 9.37 | 0.4515 | 1.50 |
| 128 | 0.8545 | 1321.0 | 48.97 | 2420 | 6557 | 8.31 | 0.4496 | 1.55 |
| 129 | 0.8552 | 1285.6 | 51.75 | 2402 | 6511 | 24.17 | 0.4477 | 1.50 |
| 130 | 0.8573 | 1261.0 | 53.91 | 2392 | 6488 | 25.51 | 0.4458 | 1.47 |
| 131 | 0.8595 | 1222.2 | 57.54 | 2374 | 6445 | 23.01 | 0.4440 | 1.42 |
| 132 | 0.8615 | 1258.9 | 54.36 | 2403 | 6512 | 12.18 | 0.4421 | 1.46 |
| 133 | 0.8625 | 1162.2 | 63.85 | 2342 | 6372 | 15.64 | 0.4400 | 1.35 |



Table 1 contains the data for PAA, studied as pure nematic; whereas Table 2 indicates the results for BOAB a pure nematic substance. The variation of the each of the physical parameters, namely, specific volume ($1/d$), ultrasonic velocity ($C$), adiabatic compressibility ($\beta$), Rao's number ($R$), Wada's constant ($B$), and the orientational parameter ($S$) as a function of the reduced temperature ($T/T_{\text{N-I}}$) in the nematic phase for PAA are shown in Fig. 1a–1e, respectively, whereas Fig. 2a–2e show the graphical representation of the same parameters in the case of the molecule BOAB.

The specific volume increases almost linearly with increase in temperature in both the molecules PAA and BOAB as shown in Figs. 1a and 2a, respectively. This value suddenly increases at the temperature corresponding to $T/T_{\text{N-I}}$ approximately equal to one. In other words, the value of the specific volume is maximum at the nematic to isotropic transition. This can be attributed to the change in the structure from the partially ordered nematic to the disordered isotropic liquid state.

The ultrasonic velocity $C$ increases as the temperature decreases in both the cases, which is clear from Figs. 1b and 2b. This probably indicates a transition from the isotropic state to the nematic state. With decreasing temperature the mean distance between the molecules also decreases and thereby the potential energy of the interaction between the molecules also decreases and thereby the potential energy of the interaction between the molecules increases, leading to increased value

**TABLE 2** The Variation of Specific Volume and Sound Velocity and Derived Quantities for PAA at Various Temp.

| $t$ (°C) | $V$ (cc/gm) | $C$ m/s | $\beta \times 10^{12}$ $cm^2$/dyne | $R$ | $B$ | $A \times 10^4$ | S | $Z \times 10^{-6}$ rayls |
|---|---|---|---|---|---|---|---|---|
| 104 | 0.9663 | 1320.9 | 55.39 | 3631 | 9659 | 19.28 | 0.4975 | 1.37 |
| 105 | 0.9673 | 1326.0 | 55.02 | 3631 | 9678 | 10.39 | 0.4955 | 1.37 |
| 106 | 0.9684 | 1319.3 | 55.64 | 3639 | 9673 | 10.65 | 0.4936 | 1.36 |
| 107 | 0.9697 | 1325.1 | 55.23 | 3637 | 9697 | 14.09 | 0.4916 | 1.37 |
| 108 | 0.9703 | 1314.1 | 56.18 | 3647 | 9679 | 5.66 | 0.4897 | 1.35 |
| 109 | 0.9709 | 1314.2 | 56.18 | 3640 | 9686 | 6.90 | 0.4877 | 1.35 |
| 110 | 0.9722 | 1309.8 | 56.67 | 3642 | 9686 | 12.82 | 0.4858 | 1.29 |
| 111 | 0.9726 | 1251.1 | 62.13 | 3643 | 9563 | 3.72 | 0.4839 | 1.34 |
| 112 | 0.9733 | 1302.0 | 57.41 | 3539 | 9679 | 7.57 | 0.4819 | 1.32 |
| 113 | 0.9748 | 1288.3 | 58.74 | 3632 | 9663 | 15.67 | 0.4800 | 1.32 |
| 114 | 0.9758 | 1286.0 | 59.01 | 3634 | 9666 | 10.30 | 0.4781 | 1.30 |
| 115 | 0.9764 | 1272.7 | 60.29 | 3624 | 9643 | 6.31 | 0.4762 | 1.31 |
| 116 | 0.9769 | 1277.8 | 59.83 | 3630 | 9657 | 4.39 | 0.4742 | 1.31 |
| 117 | 0.9775 | 1279.8 | 59.68 | 3634 | 9667 | 6.71 | 0.4723 | 1.29 |
| 118 | 0.9791 | 1266.0 | 61.09 | 3627 | 9651 | 12.81 | 0.4704 | 1.30 |
| 119 | 0.9798 | 1277.0 | 60.09 | 3640 | 9681 | 7.66 | 0.4685 | 1.30 |
| 120 | 0.9814 | 1274.4 | 60.43 | 3644 | 9689 | 16.52 | 0.4666 | 1.29 |
| 121 | 0.9820 | 1271.1 | 60.78 | 3643 | 9687 | 6.00 | 0.4647 | 1.29 |
| 122 | 0.9828 | 1267.8 | 61.15 | 3642 | 9686 | 7.50 | 0.4628 | 1.29 |
| 123 | 0.9831 | 1264.4 | 61.49 | 3640 | 9681 | 3.00 | 0.4609 | 1.28 |
| 124 | 0.9850 | 1263.0 | 61.75 | 3646 | 9694 | 19.73 | 0.4590 | 1.27 |
| 125 | 0.9873 | 1255.1 | 62.68 | 3647 | 9696 | 23.49 | 0.4571 | 1.26 |
| 126 | 0.9887 | 1249.1 | 63.37 | 3646 | 9694 | 13.82 | 0.4552 | 1.26 |
| 127 | 0.9901 | 1244.3 | 63.96 | 3647 | 9696 | 14.75 | 0.4533 | 1.24 |
| 128 | 0.9915 | 1230.7 | 65.46 | 3638 | 9677 | 13.38 | 0.4516 | 1.23 |
| 129 | 0.9922 | 1222.7 | 66.37 | 3633 | 9664 | 7.02 | 0.4496 | 1.24 |
| 130 | 0.9962 | 1233.8 | 65.45 | 3659 | 9723 | 40.81 | 0.4477 | 1.21 |
| 131 | 0.9969 | 1204.9 | 68.67 | 3633 | 9664 | 6.99 | 0.4458 | 1.16 |
| 132 | 0.9974 | 1161.3 | 73.97 | 3590 | 9566 | 4.97 | 0.4440 | 1.15 |
| 133 | 0.9986 | 1143.6 | 76.36 | 3576 | 9534 | 11.81 | 0.4421 | 1.15 |
| 134 | 0.9990 | 1198.3 | 69.58 | 3634 | 9666 | 4.02 | 0.4400 | 1.20 |



in velocity of sound. The minimum value of $C$ is at the temperature corresponding to $(T/T_{N\text{-}I})$, approximately equal to one (i.e., at the nematic to isotropic transition). The sudden increase in the value of sound velocity after this transition temperature indicates that the intermolecular distance (isotropic phase) increases, thereby decreasing the potential energy and thus increasing the observed $C$ value. It may be noted that this effect occurs predominantly in the cases of PAA and BOAB.

The variation of adiabatic compressibility ($\beta$) and Rao's number ($R$) is represented in Figs. 1c, 1d, 2c, and 2d for the compounds PAA and BOAB, and it can be seen from the plots that in both the cases,

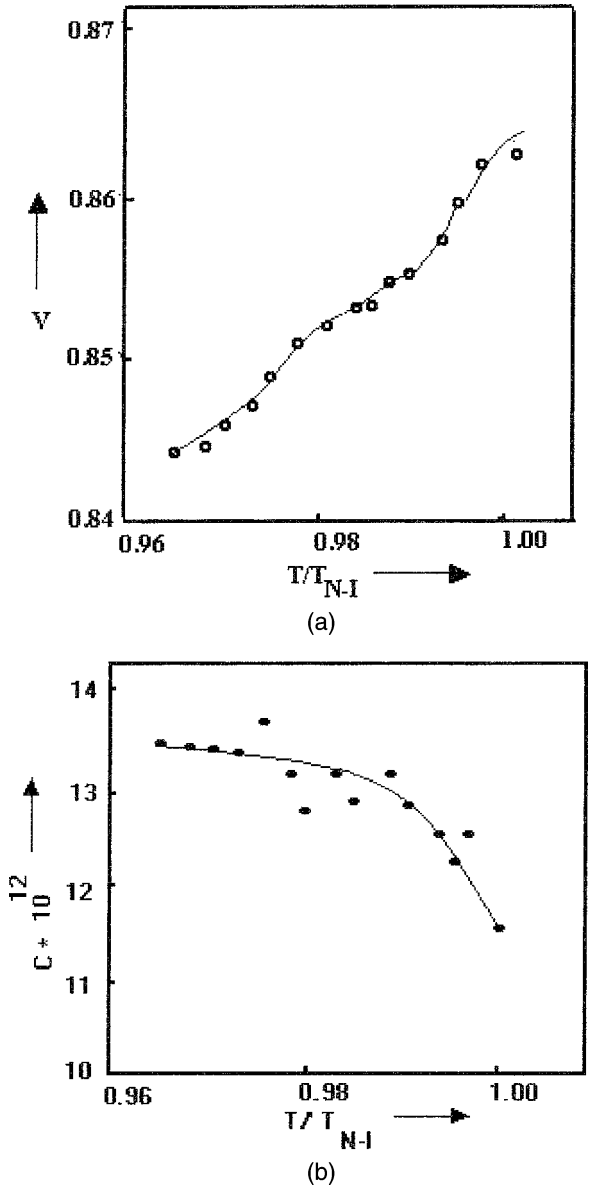
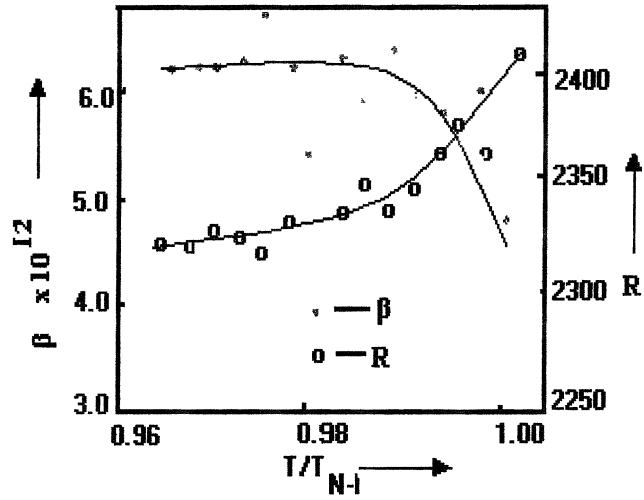
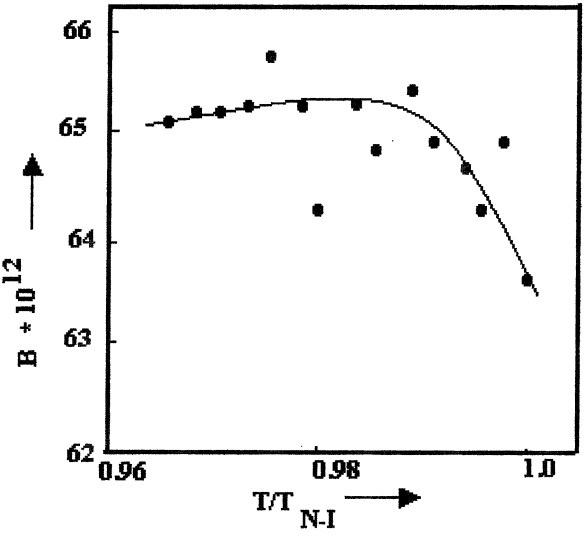



**FIGURE 1** (a) Variation of specific volume with reduced temperature; (b) variation of ultrasonic velocity with reduced temperature; (c) variation of $\beta_{ac}$ and R with reduced temperature; (d) variation of B with respect to reduced temperature; (e) variation of order parameters with reduced temperature.




(c)




(d)

**FIGURE 1** Continued.

$\beta$ increases with temperature and reaches a maximum value at the temperature corresponding to $(T/T_{\text{N-I}})$, approximately equal to one (i.e., at the nematic to isotropic transition), whereas the Rao's number attains the minimum value at this point. This observation is consistent with earlier observations [4–14].

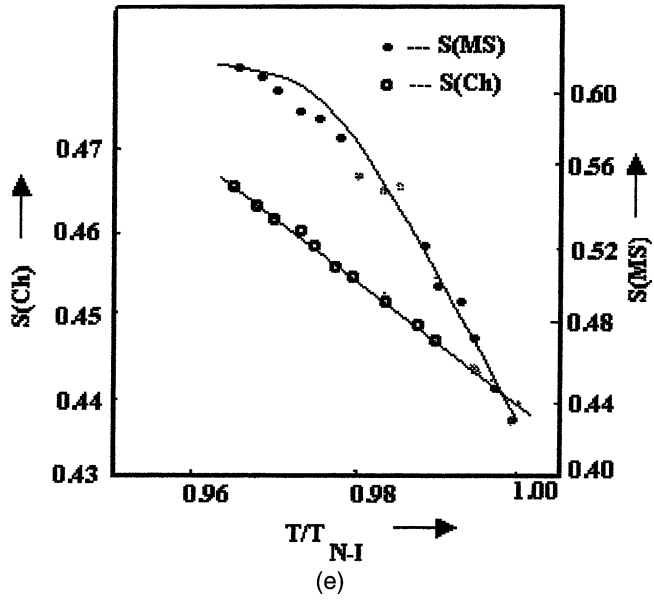



**FIGURE 1** Continued.

The variation of molar compressibility ($B$) is reported in Figs. 1d and 2d for the two samples under study. It can be seen from the figures that $B$ remains constant (especially in the case of PAA) as the temperature increases but suddenly decreases around $(T/T_{\text{N-I}}) \approx 1$. At temperatures above $(T/T_{\text{N-I}}) > 1$ (i.e., in the vicinity of the isotropic phase) $B$ increases, which is not in line with other similar systems under study [11]. The order parameter $S$ is estimated using the Maier–Saupe equation as well as Chandrashekhar's relation. The graphical representations of both, as a function of reduced temperature, are given in Figs. 1e and 2e for PAA and BOAB, respectively. A gradual fall in the value of $S$ of both types is observed with increases in temperature for both the systems, with the fall being more rapid in the value of $S$ because of Maier–Saupe.

The values of $B$, $\beta$, and $R$ do not show any definite trend of variation with temperature, particularly in the interval $(T/T_{\text{N-I}}) = 0.92$ to 0.95. This is because there is a structural change in the process of heating: fully ordered (crystal) to quasi ordered (nematic) to disordered (isotropic) phase. Most of the properties of physical parameters can be explained on the basis of Frenkal's heterophase fluctuation theory. According to this theory, as the temperature of the first-order transition is approached, an ever-increasing concentration of small

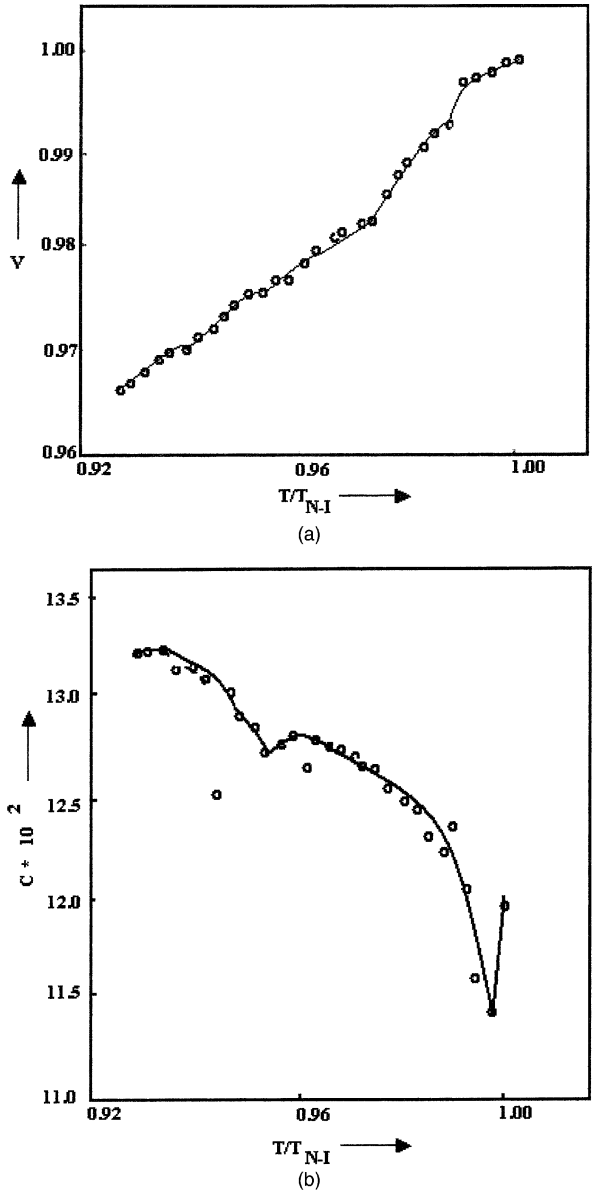



**FIGURE 2** (a) Variation of specific volume with reduced temperature; (b) variation of ultrasonic velocity with reduced temperature; (c) variation of $\beta_{ac}$ and R with reduced temperature; (d) variation of B with respect to reduced temperature; (e) variation of order parameters with reduced temperature.

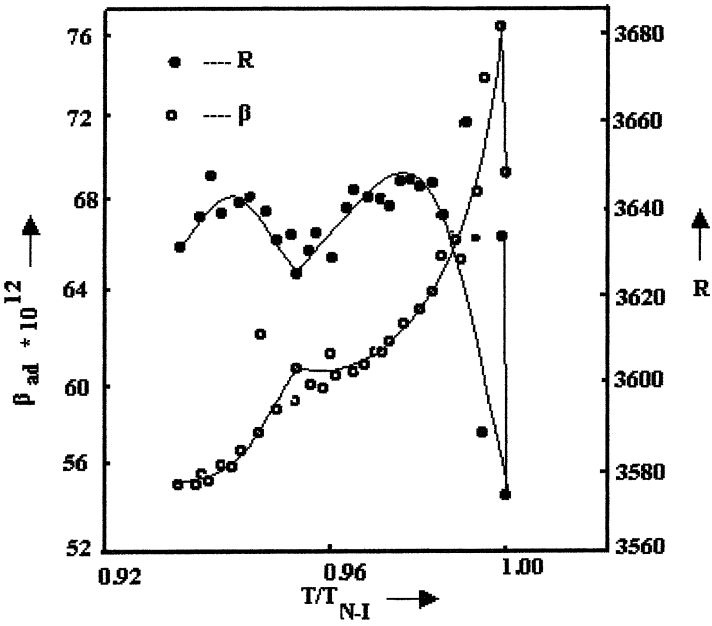



**FIGURE 2** Continued.

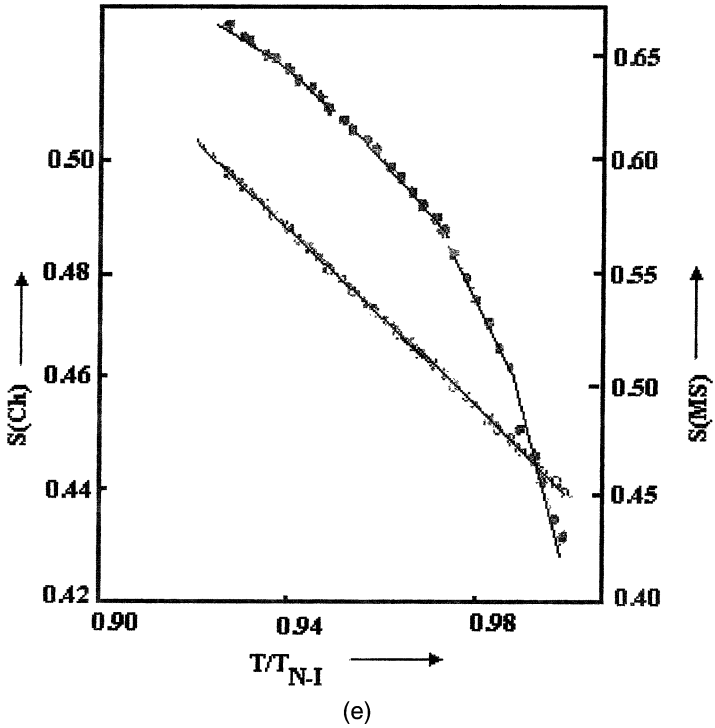



**FIGURE 2** Continued.

elements of second phase can exit in the first phase. This may lead to rigorous fluctuations resulting in pre-transitional vibrations in all the physical properties. In the present work for the values of $(T/T_{\text{N-I}}) = 0.95$ to 1.00, for the molecules studied, the variation of the parameters can be explained on the basis of theory, but for $(T/T_{\text{N-I}}) = 0.92$ to 0.95 the values fluctuate to a large extent, and this behavior seems difficult to account for. However, such observations are available in literature [15].

Further, from these observations, it may be noted that although the variation of different parameters with respect to the reduced temperature is not systematic over the whole range of reduced temperature (the lines in the figures are drawn as indicative of trend of variation of parameters with respect to the reduced temperature), it is very clear that around $(T/T_{\text{N-I}}) = 1.00$, both the systems show a clear phase transition, with transition temperature being K —— 119°C —— N —— 133°C —— I for PAA and K —— 104°C —— N —— 134°C —— I for BOAB. The figures for BOAB, especially the variation in the parameters $B$, $\beta$,

and $R$ with reduced temperature, may give the impression that there is more than one phase transition involved: however, this cannot be ascertained because this trend may be due to the combined effect of pretransitional vibrations (Frenkal's heterophase fluctuation theory, discussed in earlier paragraphs) and the errors involved in the measurements. Because the order of values in these parameters may be too large, the small variations may lead to large variations in the parameters reported. When the value of order parameters is small, the same variations are not seen, which is inconsistent with previous observations.

In the present work, the variation of different parameters in the entire range of temperature, namely, K-N-I transitions, could not be mapped because of certain experimental difficulties well below K-N transition and higher temperatures above N-I transition; however, this has not gotten in the way of this study, which is intended to be carried out around the phase transition.

All the parameters mentioned in the section Defining Relations are not discussed. The left-out parameters follow the same trend of one of the parameters discussed, as they are dependent on those parameters or to some powers of the parameters.



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