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Phase Transition Studies in N(p-n-Heptyloxy Benzylidene)p-Toluidine, 70.1, Across I-N, N-S_A and S_A-S_B Phases

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The results of density and ultrasonic velocity variation with temperature in N(p-n-heptyloxy benzylidene)p-toluidine, HYBT, 70.1 exhibiting nematic, smectic-A and crystalline smectic-B phases, are presented. The isotropic—nematic, nematic—smectic-A phase transitions are found to be first order while the smectic-A crystal smectic-B transition is weak first order. The thermal expansion coefficient α computed from the molar volume data is presented. The molar sound velocity and molar compressibility of HYBT computed from the density and ultrasonic velocity data in isotropic phase are compared with the values of the other compounds in a homologous series. They are found to be in good agreement with theory.

INTRODUCTION

The nematic to smectic-A phase transformation in liquid crystals is the subject of recent experimental[1-5] and theoretical[6-8] study in the last decade. McMillan[6] and Kobayashi[7] pointed out that this transition is either first order or second order. The focus of this interest is due to proposed analogy[9] with super conducting or superfluid transition of XY model (the lambda transition in ^{4}He). While Lubensky[8] has critically reviewed the current status of the theory of the N-A transition and made comparisons with experiment, Johnson[5] discussed

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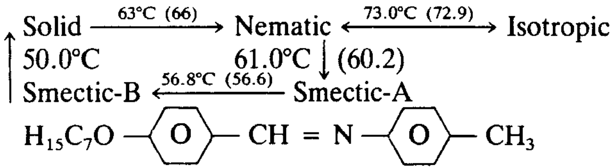
N-A tricritical point extensively and concluded that a careful study of critical exponents in a homologous series and appropriate mixtures that covers a wide range of values of T_{NA}/T_{NI} is needed to lead to concurrent theoretical and experimental situation. Recent experimental studies on 40.8 and 40.7 at MIT[2,3] indicated second order N-S_A transition using heat capacity, high resolution x-ray study and light scattering methods. Thoen et al[1,4] reported first order N-S_A transition in mixtures of 9CB and 10CB possessing narrow nematic region i.e., when $T_{NA}/T_{NI} \rightarrow 1.000$ and second order transition in pure compounds possessing $T_{NA}/T_{NI} < 0.994$. The order of the phase transition for the smectic-A to nematic and the other smectic—smectic or nematic to isotropic transformations, can also be studied by density[10,11] and ultrasonic velocity[12-14] variation with temperature. Most of the recent work on the order of the S_A-N transformation studies is carried out mainly on the three homologous series of compounds (1) highly polar compounds exhibiting bilayer structural arrangement in the smectic-A phase viz., p-n-alkyl or p-n-alkoxy cyanobiphenyls (2) weakly polar compounds viz., N(p-n-alkoxy benzylidene)p-n-alkylaniline, no.m.compounds and (3) 4-n-pentyl phenyl thiol-4′-alkoxy benzoates. Relatively the experimental results at the S_A-N transition in non-polar and weakly polar compounds are meagre which prompted to carry out the present work and it describes the density and ultrasonic velocity variation with temperature in N(p-n-heptyloxy benzylidene)p-toluidine, HYBT, (70.1). HYBT, a weakly polar compound, exhibits enantiotropic nematic phase and monotropic smectic-A and smectic-B phases.

The molar volume, molar sound velocity and molar compressibility are compared and discussed with the values of the other members in this homologous series.

EXPERIMENTAL

HYBT was prepared by condensation of p-n-heptyloxy benzaldehyde and p-toluidine in refluxing absolute ethanol for four hours in presence of a few drops of glacial acetic acid and after removing the solvent the crude N(p-n-heptyloxy benzylidene)p-toluidine was repeatedly recrystallised from absolute ethanol to give a pure white crystalline sample exhibiting constant transition temperatures which are in agreement with literature values. The transition temperatures, presented below are confirmed by thermal microscopy. The literature values[15] are given in parentheses.



N(p-n-heptyloxy benzylidene) p-toluidine

The density measurements were carried out using a bicapillary pyknometer[10] and the ultrasonic velocity measurements[14] were carried out at a frequency of 2MHz using the ultrasonic interferometer UF 101 N.P.L., India with slight modifications. The absolute accuracy in temperature measurements is ±0.1°C while the relative accuracy is ±0.025°C. The accuracy in ρ is ± 0.1 Kg.m^{-3}, while the ultrasonic velocity measurements are accurate to ±0.1%. The rate of cooling is 0.1°C per hour.

RESULTS AND DISCUSSION

The results of the density and ultrasonic velocity variation with temperature in HYBT in the isotropic, nematic, smectic-A and smectic-B phases are illustrated in Figures 1 and 2.

The compound exhibits only a nematic phase in heating while on cooling the sample exhibits smectic-A and smectic-B phases in addition to the nematic phase before finally becoming solid phase.

The density (Figure 1) and ultrasonic velocity (Figure 2) in the isotropic phase linearly increases with the decreasing temperature as in other liquids. No hysteresis was observed in density in the heating and cooling cycles. A smooth change in density is seen over a range of 2°C for a cooling rate of 2°C per hour. However a jump is observed when the rate of cooling is 0.1°C per hour. A sudden jump in density $(\Delta\rho/\rho) = 0.2\%$ and an anomalous decrease in the ultrasonic velocity (Figure 2) are observed at the nematic-isotropic transition temperature. The transition temperature observed by these methods coincides with that observed by the thermal microscopy within 0.1°C. The thermal expansion coefficient is calculated from the relation $\alpha = (1/M_V)(dM_V/dT)$ where M_V is the average molar volume and dM_V is the molar volume difference across the temperature difference dT. The thermal expansion coefficient (Figure 3) maximum at this transition temperature suggests a first order nature of this transition. The pretransitional effects are found to occur both in the density and ultrasonic velocity measurements across the transition. The range of

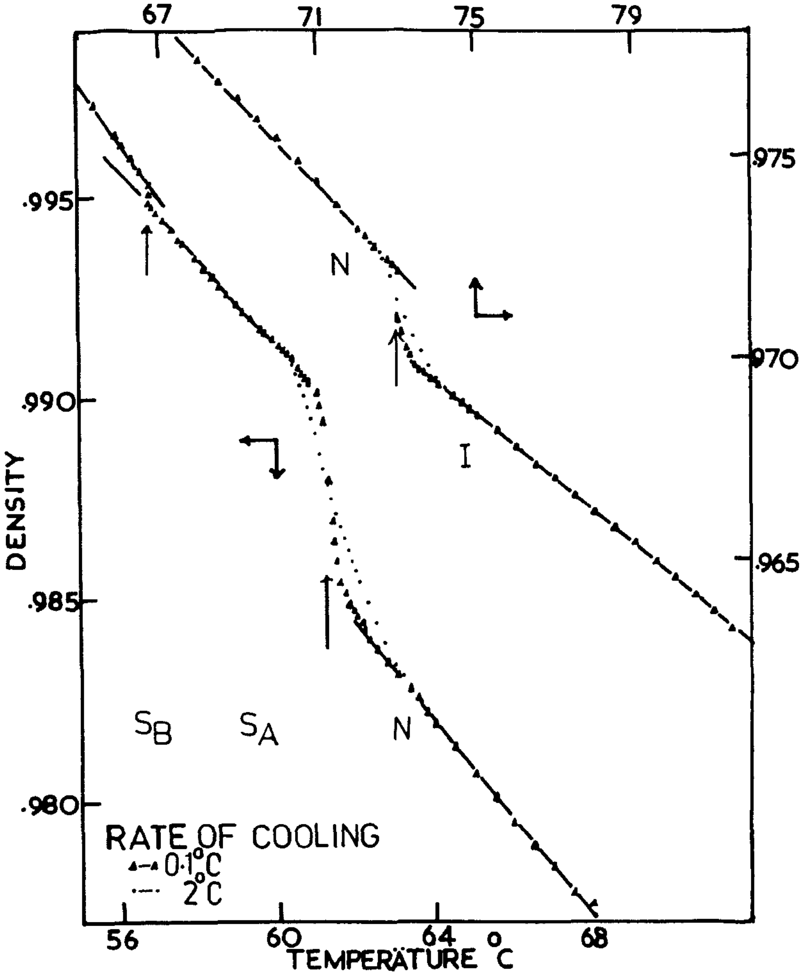


FIGURE 1 Variation of density, $\rho(10^3\ \mathrm{kg \cdot m^{-3}})$ with temperature in S_B, S_A, N and Isotropic phases in HYBT.

the pretransitional effects observed are 0.4°C and 1.3°C in the density and ultrasonic velocity experiments respectively. The anomalous decrease in the ultrasonic velocity is 2.83% in comparison with the normal linear temperature dependence.

The density jump across this transition is in agreement with the reported data across the N-I transition in other samples.[16-17] However the density jump is found to be smaller than the values reported for other members of this homologous series.[18-21]

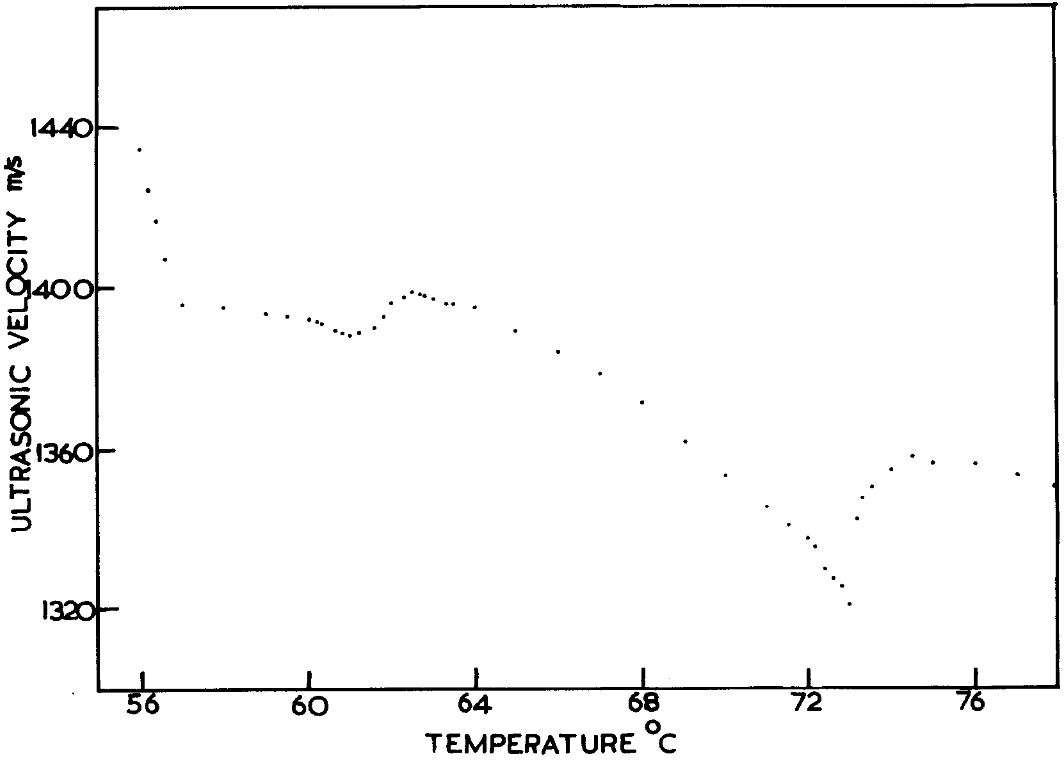


FIGURE 2 Variation of ultrasonic velocity with temperature in HYBT.

The calculated molar volume, from the density and its molecular weight of N(p-n-heptyloxy benzylidene)p-toluidine along with the reported molar volumes of the other members of the homologous series at temperatures above and below the nematic—isotropic transition temperature are presented below.

	Molar volume ($m^3 \times 10^6$)		
	$(T_{NI} - 3)$°C	$(T_{NI} + 3)$°C	Reference
N-(p-n-pentyloxy benzylidene) p-toluidine (PBT)	283.26	285.70	15
N-(p-n-hexyloxy benzylidene) p-toluidine (HBT)	300.19 299.65	303.06 302.87	12 13
N-(p-n-heptyloxy benzylidene) p-toluidine (HYBT)	317.21	319.76	present work
N-(p-n-octyloxy benzylidene) p-toluidine (NBT)	351.63	354.92	14

If additivity of atomic volumes is assumed, the calculated contribution for a single methylene group from the difference in the molar volumes of N(p-n-alkoxy benzylidene) p-toluidines at $(T_{NI} + 3)$°C from one another in isotropic phase is $17.14 \pm .44 \times 10^{-6}$ m^3/mol. In the nematic phase of these compounds at $(T_{NI} - 3)$°C the calculated molar volume for a CH_2-unit is found to be $16.75 \pm 0.35 \times 10^{-6}$ m^3/mol. This value of CH_2 unit in the nematic phase is lower than the contribution of a methylene group in n-alkylbiphenyls isotropic phase (17.1×10^{-6} m^3/mol)[22] and is substantially higher than in n-alkanes in the solid state (14.5).[23] These results indicate that the packing of alkyl groups (as well as that of the central aromatic cores of the molecules) in the nematic phase is closer to packing in the isotropic phase than in the solid phase. Also the —(CH_2)— unit contribution in the nematic phase is smaller than in the isotropic phase and it indicates the closer packing of the molecules in the nematic phase than in the isotropic phase.

The smectic-A to nematic transition is considered to be very interesting because of its close analogy to ^{4}He lambda transition and the controversy regarding the order of the transition inferred from different experimental results.[24–26]

The maximum density jump that occurs across the S_A-N transition is, $\Delta\rho/\rho = 0.46\%$ and is higher than the values observed at the N-I and S_A-S_B transitions. The pretransitional effects which are present on both sides of the transition ranges for 2.6°C for a cooling rate of 2°C per hour and are however predominant on the nematic side of the transition. When the experiment is repeated at a cooling rate of 0.1° per hour the pretransitional effects are considerably reduced and the whole 3 ml of opaque nematic phase in the bulb transforms into translucent smectic A phase within 0.5°C. The transition temperature observed through thermal microscopy, coincides with the temperature where thermal expansion coefficient is maximum and the ultrasonic velocity is minimum. The pretransitional effects are present in the nematic side of the transition. The ultrasonic velocity shows anomalous behaviour at the S_A-N transition. The anomalous decrease in the ultrasonic velocity is 0.79% and the range of anomalous behaviour is 1.5°C. The thermal expansion coefficient maximum, (Figure 3) which is higher than the $\alpha_{N\text{-}I}$ and $\alpha_{S_A\text{-}S_B}$, density jump and anomalous drop in ultrasonic velocity indicate a first order S_A-N phase transition.

From the X-ray results,[15] the molecular length (1 = 23.5 ± 0.5 Å) and layer spacing (23.7 ± 0.02 Å) in the smectic-A phase, which are of the same order, indicate a monolayer molecular arrangement in the S_A phase. The nematic phase is characterised by the long-range orientational order with molecular diffusion. In the smectic-A phase, in addition to the long-range orientational ordering, the molecules are averaged in layers, a one-dimensional periodic ordering with their long axes, on average, to the layer normal. The nematic to smectic-A transition involves the establishment of ordered structure involving orientation is being formed i.e., discontinuity in molecular diffusion. The monolayer molecules need more volume per unit molecule than the bilayer molecules because of aliphatic end chain diffusion. Hence a transition from nematic to smectic-A phase possessing monolayer molecular arrangement involves larger volume change than the nematic to smectic-A phase possessing bilayer molecular arrangement. The observed experimental results confirming a first order transition can explain this fact. However in higher homologues[27] 50.8 and 50.10 which exhibited N-A transition, we found no sudden jump in density. At present the explanation we can offer is the end aliphatic chains can overlap in lengthy molecules like 40.8, 50.8 and higher homologues, thereby occupying comparatively smaller volume than their all trans configuration requirement.

The predominant pretransitional effects on the nematic side at the N-S_A transition can be explained as follows. It is reported[28] that the time required for the establishment of equilibrium, when an ordered structure involving orientation is being formed, is much larger than the time required to disrupt it. The pretransitional effects are found to be larger in the achievement of equilibrium for a slow growing smectic-A phase from the nematic phase above the N-A transition than consolidating the established stocks of smectic-A layers in the smectic-A phase below the transition.

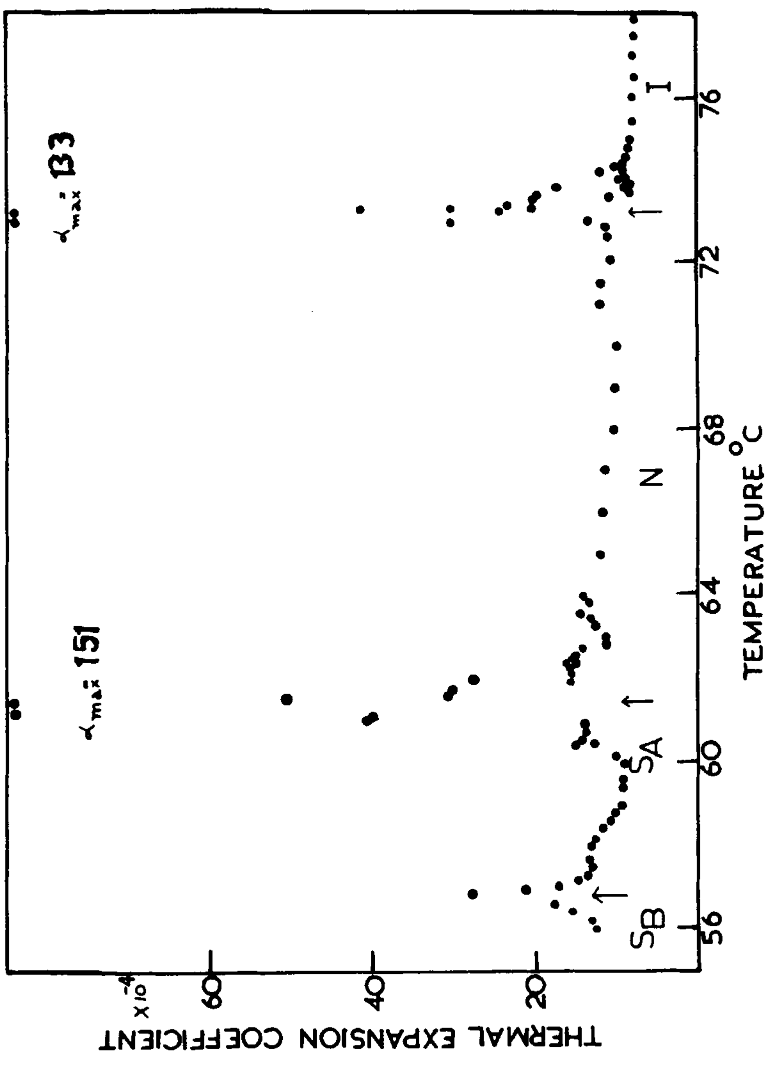


FIGURE 3 Variation of thermal expansion coefficient, $\Phi(°C^{-1}\cdot 10^{-4})$ with temperature in HYBT.

The first reports of S_A-N phase transition in N(p-cyano benzylidene)p-n-octyloxy aniline (CBOOA) [$\Delta v = (0.5 \pm 0.2) \times 10^{-4}$ m^3/Kg] and p-n-octyl p'-cyano biphenyl (8CB)[25] ($\Delta v/v = 0.06\%$) by volumetric studies confirmed first order phase transition. However, precision volumetric studies by Armitage and Price[24] reapprised the order of the S_A-N transition in CBOOA as second order and assigned the earlier observation of Torza and Cladis,[30] is due to pretransitional effects. Similarly heat capacity[1,26] and light scattering experiments[29] in 8CB and other highly polar compounds confirmed the S_A-N transition as second order. Incidentally all the polar compounds possess bilayer molecular arrangement and exhibit second order S_A-N transition, even though their McMillan parameter is far above 0.88 to predict first order transition.

In weakly polar compounds exhibiting N-S_A transition the situation is different. In terephthalylidene bis(p-n-butyl aniline) TBBA, ($T_{NA}/T_{NI} = 0.92$) high precision ultrasonic velocity studies[12,30] inferred the N-S_A transition as first order. The density[31] results also indicated a first order transition ($\Delta\rho/\rho = 0.16\%$). Our earlier results in other Schiff's bases by density and ultrasonic velocity measurements confirmed the N-S_A transition as first order.

The smectic-A to smectic-B transition at 56.8°C is also of interest because of a very small change in density and a significant change in ultrasonic velocity with temperature below this transition. The density change across this transition $\Delta\rho/\rho$ is 0.05% and the ultrasonic velocity which attains flat region in the S_A phase suddenly increases in S_B phase below this transition. However, no anomalous decrease in ultrasonic velocity is observed at this transition. Bhattacharya *et al.*,[32] reported pretransitional flattening at the S_A-S_B transition, in β-methylbutyl p(p-methoxy benzylidene)amino cinnamate, in ultrasonic velocity at 4 MHz for perpendicular propagation. Previously in N(p-n-hexyloxy benzylidene)p-n-butyl aniline (HBBA)[33] and N(p-n-octyloxy benzylidene)p-n-butyl aniline (OBBA)[33] a sharp dip in the ultrasonic velocity at S_A-S_B transition is observed. However, the variation of the ultrasonic velocity with temperature in this sample resembles the variation in HBBA. The small change in density, absence of anomalous change in ultrasonic velocity and a maximum in thermal expansion coefficient at this transition suggest a weak first order S_A-S_B transition. The textural observation through thermal microscopy confirms the B phase as crystalline smectic-B, by the appearance of transition bars across the fans at the S_A-S_B transition and a clear focal conic fan texture on cooling, which resembles the characteristic crystalline smectic B texture of OBBA.[34]

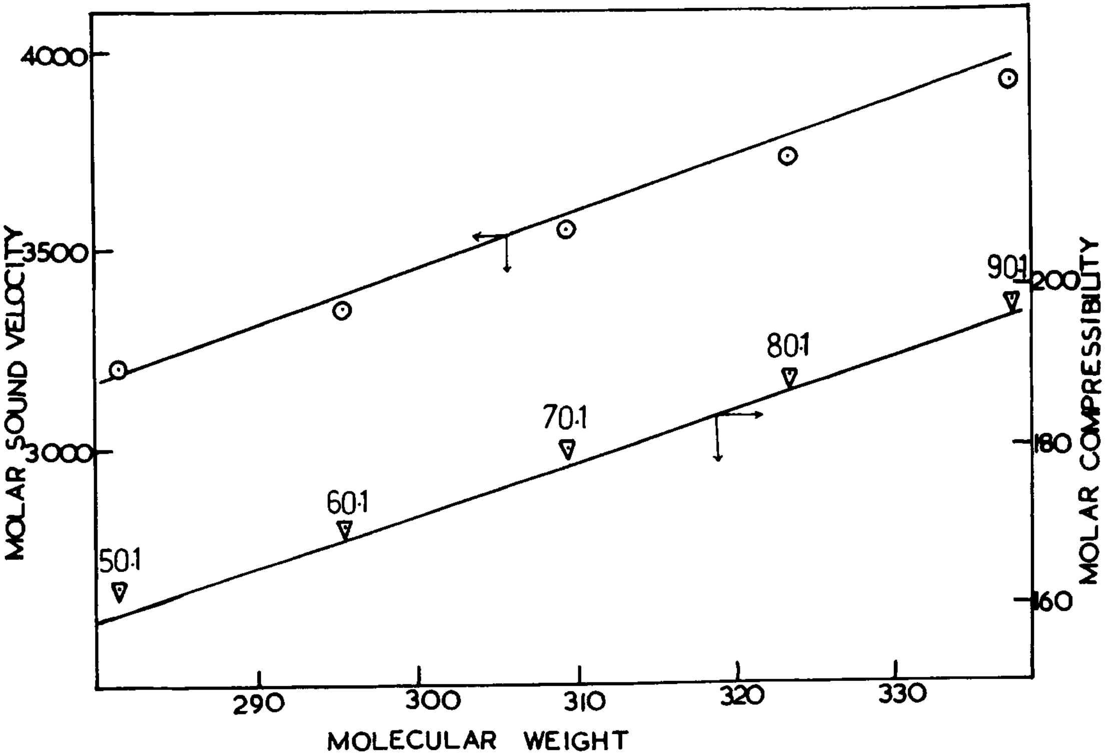


FIGURE 4 Variation of molar sound velocity R_n (10^{-6} $m^{10/3}$ $S^{-1/2}$) and molar compressibility, A_w ($10^{-31/7}$ $m^{20/7}$ $kg^{1/7}$ $S^{-2/7}$) in isotropic phase with molecular weight. Solid lines represent theoretical graphs. Molar sound velocity theoretical graph from Ref. 35. Molar compressibility theoretical graph from Ref. 36.

The adiabatic compressibility, β_{ad}, molar sound velocity, R_n, and molar compressibility, A_W, are computed using the density and ultrasonic velocity results from the following equations in the isotropic phase.

$$\beta_{ad} = v/V^2$$

$$R_n = M_v \cdot V^{1/3}$$

$$A_W = M_v \cdot \beta_{ad}{}^{-1/7}$$

where $v = (1/\rho)$, is the specific volume, $M_v = v \times M$, M_v is the molar volume, M = molecular weight and V = ultrasonic velocity.

The molar sound velocity[35] and molar compressibility[36] are two important physical constants that can be derived from density and ultrasonic velocity. They are related to the molecular structure of the compounds. In the isotropic liquids Rao[35] and Wada[36] characterised the constants molar sound velocity, R_n, and molar compressibility, A_W, by the additivity of atomic and bond increments respectively. Both R_n and A_W were found to be independent of temperature in unassociated liquids. In the mesomorphic phases it is found that the situation is quite different. Both molar sound velocity and molar compressibility are found to be almost constant with temperature in the isotropic phase. In the isotropic phases the molar sound velocity and molar compressibility are found to be constant for all the compounds reported. It is also found that they follow the additivity rule within a homologous series. The molar sound velocity and molar compressibility variation with increasing molecular weight within a homologous series in isotropic phase is shown in Figure 4. The experimental values are in good agreement with the theoretical values[35,36] and for every additional (CH_2) group contribution the molar sound velocity and molar compressibility change by almost the same amounts.

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