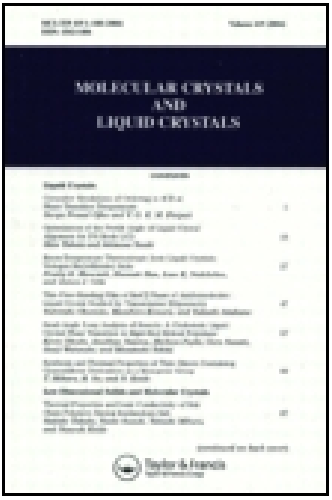

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Investigation of Ultrasonic Velocity and Related Parameters in Liquid Crystalline Mixtures

A. K. George [a] , R. A. Vora [b] & A. R. K. L. Padmini [a]
[a] Applied Physics Department, Faculty of Technology and Engineering , M.S. University of Baroda , Baroda, 390 001, India.
[b] Applied Chemistry Department, Faculty of Technology and Engineering , M.S. University of Baroda , Baroda, 390 001, India.

To cite this article: A. K. George , R. A. Vora & A. R. K. L. Padmini (1980) Investigation of Ultrasonic Velocity and Related Parameters in Liquid Crystalline Mixtures, Molecular Crystals and Liquid Crystals, 60:4, 297-310, DOI: 10.1080/00268948008071439

To link to this article: http://dx.doi.org/10.1080/00268948008071439

Mol. Cryst. Liq. Cryst., 1980, Vol. 60, pp. 297–310
0026-8941/80/6004-0297$04.50/0

Printed in the U.S.A.

Investigation of Ultrasonic Velocity and Related Parameters in Liquid Crystalline Mixtures

A. K. GEORGE, R. A. VORA,† and A. R. K. L. PADMINI
Applied Physics Department, Faculty of Technology and Engineering, M.S. University of Baroda, Baroda-390 001, India.

(*Received July 19, 1979; in final form December 27, 1979*)

Investigations of ultrasonic velocity, specific volume and related parameters were carried out in a mixture of *p*-*n*-butoxybenzylidene-*p*-chloroaniline (BBCA) and *p*-anisal-*p*-toluidine (*p*A*p*T) at eight different concentrations. BBCA exhibits polymorphism with two smectic phases, viz., smectic B and smectic A, while *p*A*p*T is non-mesomorphic. All the mixtures studied were nematic, the mesomorphism vanishes below 34.3 mole percent of BBCA. Specific volume showed a large increase in the vicinity of the phase transition and the ultrasonic velocity showed an abrupt minimum near the transition. The adiabatic compressibility showed a maximum near the phase transition. It was found that the dip in ultrasonic velocity, change in specific volume and the jump in adiabatic compressibility at the transition decreases with increasing concentration of the non-mesomorphic compound. The parameter, viz., molar sound velocity was also estimated. The coefficient of thermal expansion and adiabatic compressibility were also estimated and they were found to attain very high values near the phase transition. The experimental results are explained on the basis of de Gennes theory of pre-transitional effects generalized by Bendler. The critical exponents are estimated in the isotropic as well as in the nematic phases.

INTRODUCTION

In recent years, the study of the physical properties of liquid crystalline fluids by ultrasonic methods is developing at a rapid rate. The recent reviews by Candau and Letcher[1] and Natale[2] incorporates most of the work done on ultrasonic studies in liquid crystals. Compared to the work on ultrasonic studies in pure liquid crystals, the studies on liquid crystalline mixtures is scanty. Padmini *et al.*,[3,4] Dyro and Edmonds[5] and Nagai *et al.*[6] studied temperature dependence of ultrasonic properties of some mixed liquid crystals at various concentrations.

---

† Applied Chemistry Department.

Vora and Chhangawala[7] obtained the phase diagram for a binary system of smectogenic BBCA and non-mesogenic *p*A*p*T. They observed that the presence of a small amount of non-mesogenic compound changes the parent smectogenic into a nematogenic. This type of novel behaviour in mixed mesomorphism where a smectic mesophase is converted into a nematic mesophase by the addition of a non-mesogenic Schiff's base is quite an interesting observation from the view point of utility and also for the understanding of smectic mesophase. Accordingly, the above mixture was chosen for a systematic investigation of ultrasonic velocity, specific volume and other related parameters at various concentrations. As the specific volume jump and ultrasonic velocity dip at the mesophase-isotropic transition temperature of the liquid crystals are characteristic of the liquid crystalline nature of the compound, the authors have proposed to study the above parameters in this liquid crystalline mixture to explore how the addition of the non-mesogen to the mesogen affect the liquid crystalline nature of the parent compound. Further, the object of the investigation is to study the pre-transitional effects at various concentrations and their variation with increasing concentration of the non-mesogen.

EXPERIMENTAL

p-*n*-Butoxybenzaldehyde was prepared by the method of Gray and Jones.[8] The Schiff's base from *p*-*n*-butoxybenzaldehyde and *p*-anisaldehyde was prepared by condensing equimolecular quantities of these aldehydes with respective substituted anilines. The liquid crystalline mixtures were prepared according to the method of Kartha and Padmini.[4] The transition temperatures were measured using a thermopan polarizing microscope equipped with a Mettler FP–2 heating stage.

The velocity measurements were carried out using fixed path double crystal interferometer developed by Rao and Rao.[9] The interferometer was suitably modified for velocity measurements in liquid crystals. The densities were measured by a special dilatometer constructed for this purpose.[10] The temperature was controlled to ±0.05°C using a mercury-nitrobenzene thermostat along with an electronically operated relay. The velocity measurements are accurate to 1 m/sec and the densities to 0.0001 gm/cc.

RESULTS AND DISCUSSION

The pure smectogen BBCA and non-mesogen *p*A*p*T and their mixtures which exhibit nematic mesophase at eight different concentrations were studied. The concentrations of the mixtures studied were as given in Table I.

TABLE I

Concentration in mole % of BBCA + *p*A*p*T mixture

Mix. No.	Mole % of BBCA	Mole % of *p*A*p*T
1	93.7	6.3
2	87.6	12.4
3	75.8	24.2
4	64.7	35.3
5	54.0	46.0
6	43.9	56.1
7	34.3	65.7
8	25.1	74.9

From the velocity and density measurements, the parameters, adiabatic compressibility (K_{ad}) and molar sound velocity (R) were estimated using the following relations.

$$K_{ad} = \frac{1}{\rho V^2} \tag{1}$$

$$R = \frac{\overline{M}}{\rho} V^{1/3} \tag{2}$$

where V is the velocity, ρ, the density and $\overline{M}$, the molecular weight of the mixture given by the relation

$$\overline{M} = \frac{n_1 M_1 + n_2 M_2}{n_1 + n_2} \tag{3}$$

where M_1 and M_2 are the molecular weights, n_1 and n_2 are the number of gram molecules of BBCA and *p*A*p*T, respectively.

The approximate values of "S," the order parameters of various nematic mixtures were estimated from the volume jumps observed at the phase transitions following Maier and Saupe's theory.[11] The value of $\Delta v_{n,k}$ was estimated by extrapolating the linear plots of the specific volume against temperature curve to the transition temperature. The ratio $\Delta v_k/v_{n,k}$ was calculated and from the theoretical curve of Maier and Saupe[11] between $\Delta v_k/v_{n,k}$ and "S," the corresponding value of "S" was determined.

Figure 1 shows the variation of V and $1/\rho$ for BBCA and *p*A*p*T. For BBCA, the ultrasonic velocity measurements were taken only in the anisotropic region and 10°C beyond transition in the isotropic region. The velocity near the transition could not be measured due to high ultrasonic absorption. The density measurements were taken throughout transition and also in the isotropic and anisotropic phases. It was found to increase near the transition over a range of 5°C. In *p*A*p*T, the ultrasonic velocity and density vary linearly with temperature, characteristic of organic compounds.

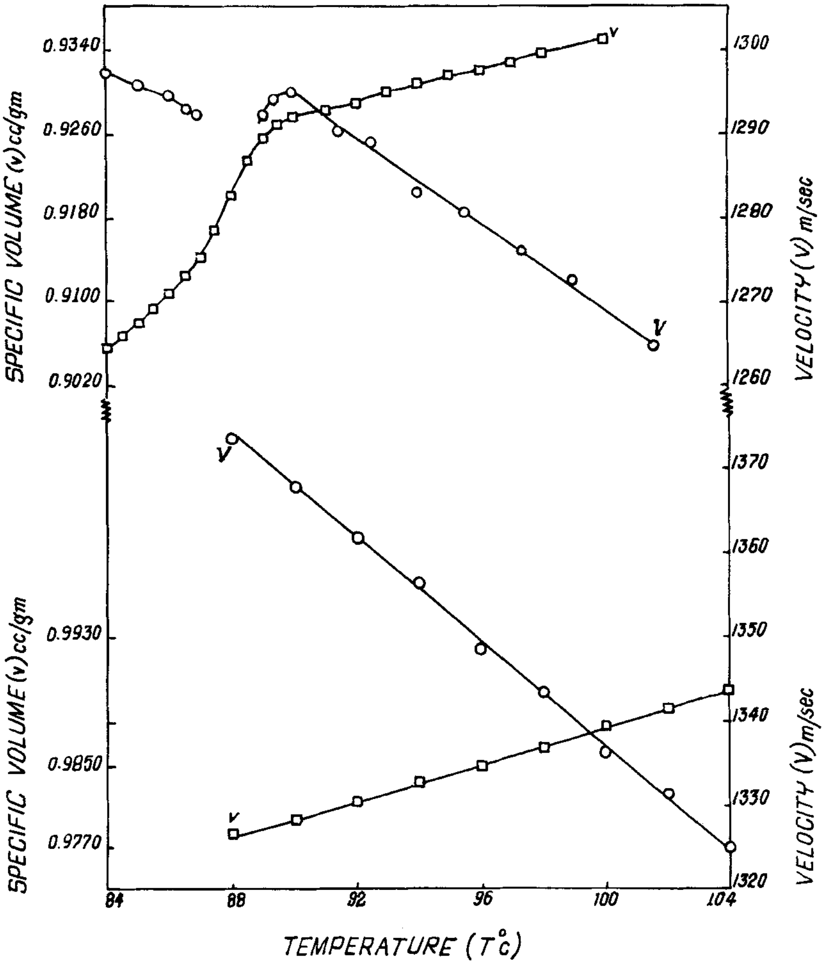

FIGURE 1 Variation of ultrasonic velocity (V) and specific volume (v) with temperature (T) for BBCA (top) and *p*A*p*T (bottom).

Figure 2 shows the variation of V, $1/\rho$ and K_{ad} for 6.3 mole percent of *p*A*p*T. The velocity is linear both in the isotropic and anisotropic regions but shows an abrupt minimum at the nematic-isotropic transition. The adiabatic compressibility shows a pronounced maximum at the transition. The specific volume varies linearly both in the isotropic and anisotropic regions away from the transition but shows a large increase at the transition. The behaviour of the mixtures containing 12.4 and 35.3 mole percent of *p*A*p*T(Figures 3 and 4) are similar to that of 6.3 mole percent of *p*A*p*T.

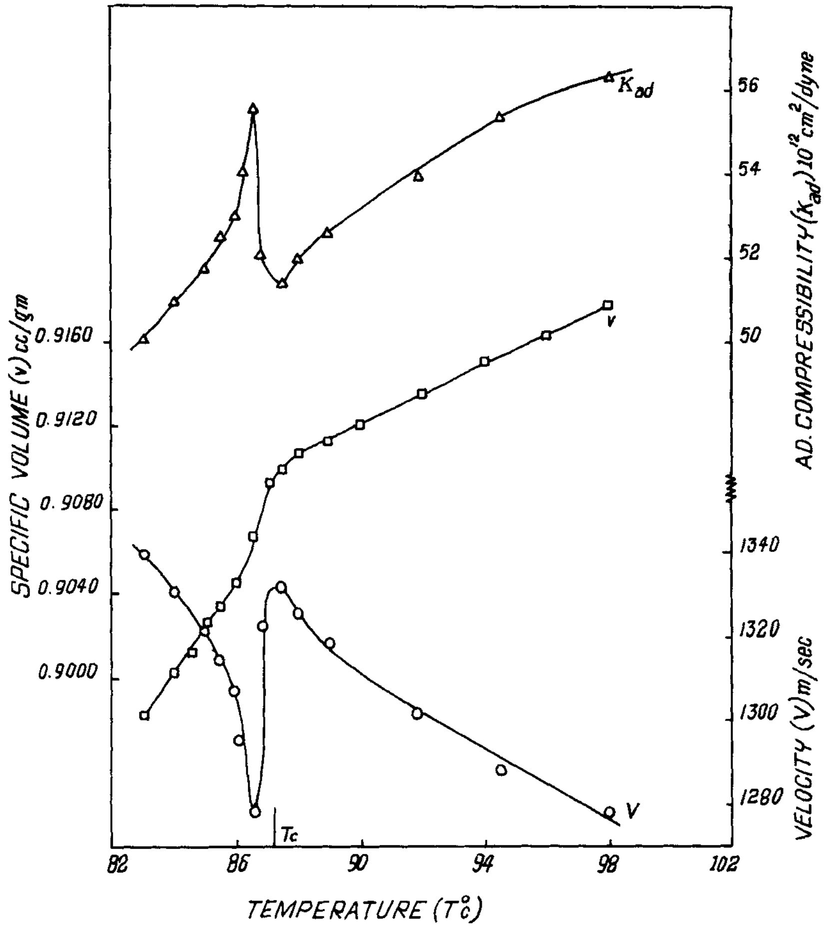

FIGURE 2 Variation of ultrasonic velocity (V), specific volume (v) and adiabatic compressibility (K_{ad}) with temperature (T) for Mix. 1.

Molar sound velocity has exhibited a behaviour similar to ultrasonic velocity by showing a dip at the phase transition of each of the mixtures. It is observed that far away from transition, both in the isotropic and anisotropic phases it remained nearly constant.

Figure 5 shows the change in ultrasonic velocity dip and adibatic compressibility jump at the transition, variation of the transition temperature and the order parameter "S," with increasing concentration of *p*A*p*T. A study of the figure reveals that the variation of the transition temperature with increasing concentration of the non-mesogenic compound is approximately linear. A comparative study of the variation of the transition temperature

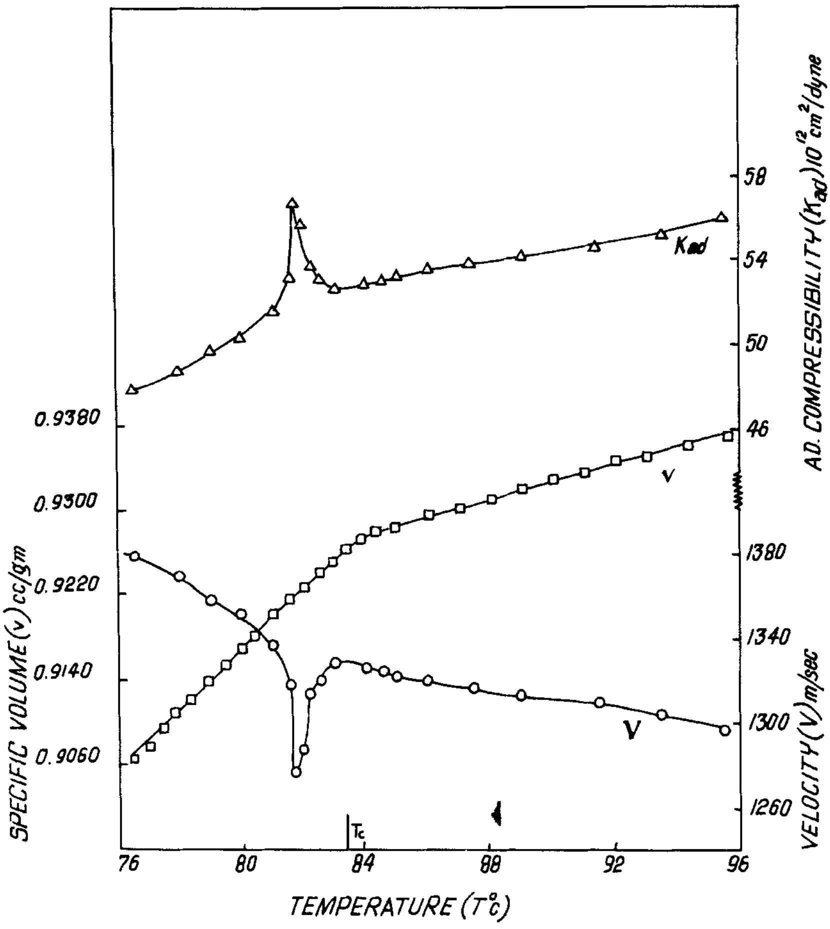

FIGURE 3 Variation of the same parameters as in Figure 2 for Mix. 2.

with increasing concentration of the non-mesogen with ultrasonic velocity dip and adiabatic compressibility jump reveal that the variation of the latter two parameters are approximately linear. Hence, it can be presumed that the velocity dip and adiabatic compressibility jump are related to the mesogenic state of the compound. Further, an approximate estimate of "*S*" (order parameter) from density measurements based on Maier and Saupe's theory[11] reveals that the order parameter initially shows a sudden drop and then decreases gradually.

In order to investigate the nature of the nematic-isotropic phase transition, the parameter $\Delta v/v$ (Δv is the change in specific volume and v is the volume at transition) was plotted against mole percent of BBCA, the mesomorphic

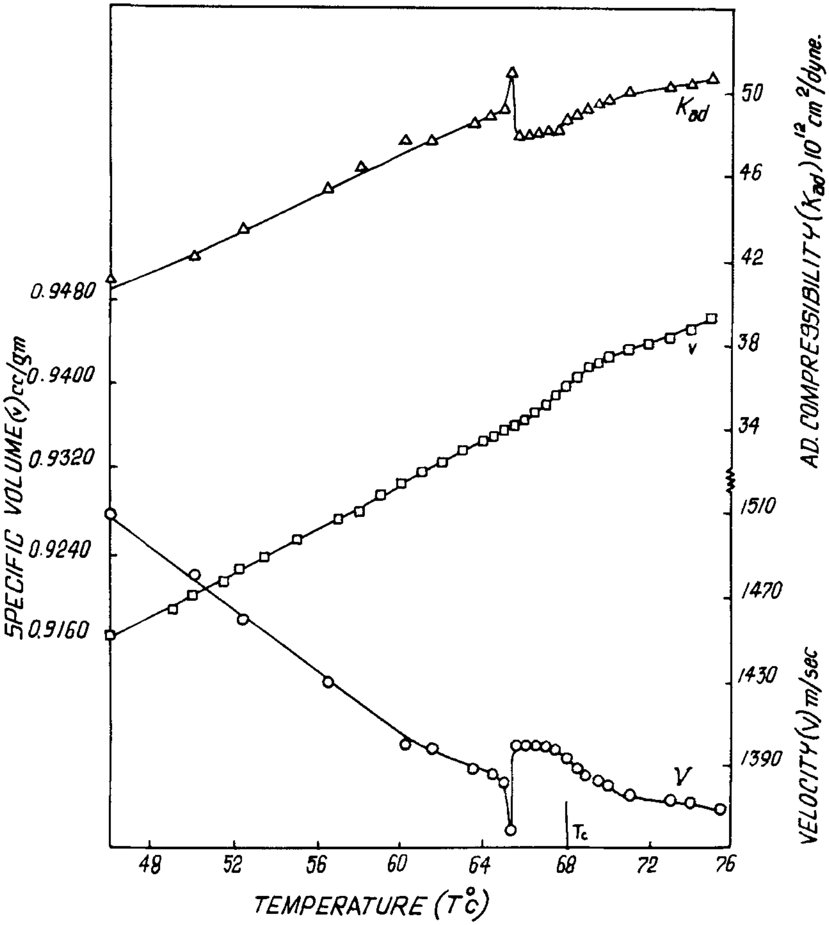

FIGURE 4 Variation of the same parameters as in Figure 2 for Mix. 3.

compound. It is interesting to note that the plot is remarkably linear passing through the origin (Figure 6). Similarly, the parameter $\Delta K_{ad}/K_{ad}$ (ΔK_{ad} is the adiabatic compressibility jump and K_{ad} is the value just after transition in the isotropic phase) was plotted against mole percent of BBCA. The plots are linear, passing through the origin. These results confirm that the nematic-isotropic transition is first order.

The parameters, thermal coefficient of expansion and temperature coefficient of adiabatic compressibility were estimated in the isotropic and anisotropic regions near the phase transition. It was observed that both the parameters attained high values near the phase transition showing the presence of pre-transitional effects. Here, an attempt has been made to

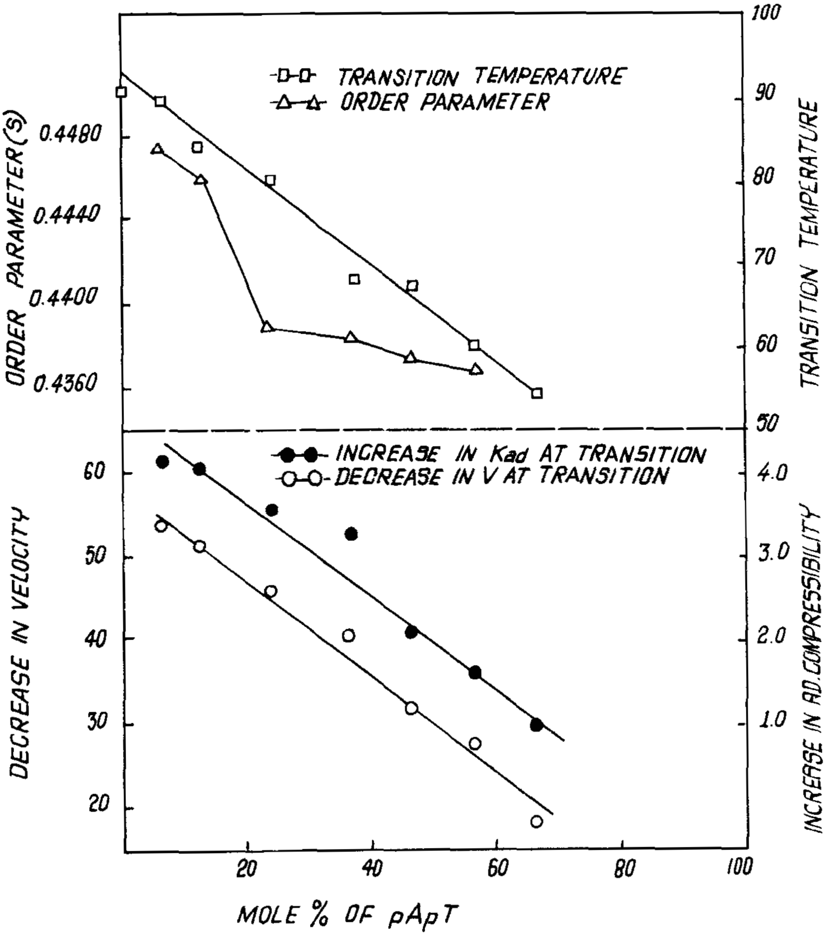

FIGURE 5 Change in velocity dip (ΔV), adiabatic compressibility jump (ΔK_{ad}) and order parameter (S) at transition and transition temperature with increasing concentration of *pAp*T.

explain this behaviour by de Gennes theory[12] of pre-transitional effects generalized by Bendler[13] and to estimate the critical exponents. Bendler[13] explained the anomalies in thermal expansion and isothermal compressibility near nematic-isotropic transition, postulating the presence of orientational fluctuations besides number density fluctuations. On this theory, he has predicted that the number density fluctuations which are governed by the order fluctuations will vary with temperature above the nematic transition as

$$(\Delta\rho)^2 \sim (T - T^*)^{-\gamma} \tag{4}$$

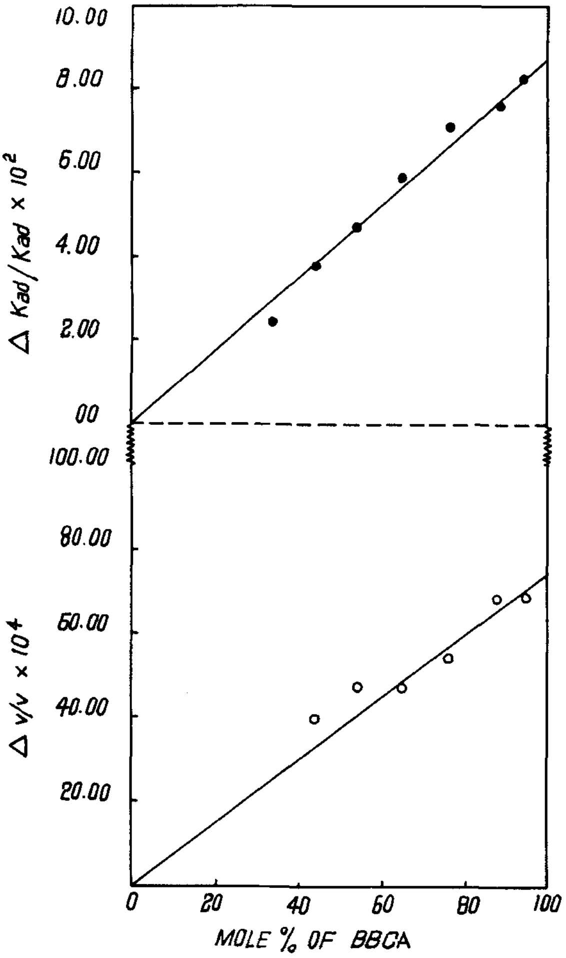

FIGURE 6 Variation of $\Delta v/v$ and $\Delta K_{\mathrm{ad}}/K_{\mathrm{ad}}$ with mole % of BBCA.

where T is the absolute temperature, T^* is the pseudocritical temperature of nematic ordering and γ is the exponent determining the growth of the order fluctuations. Light scattering and magnetic birefringence studies have shown that γ is very near to one and $(T - T^*) = 1$ for MBBA. Bendler[13] suggested that these density fluctuations produce increase in isothermal compressibility which can be expressed as

$$K_T = K_0 + C(T - T^*)^{-\gamma} \tag{5}$$

where K_T is the isothermal compressibility. He also assumed that the compressibility anomaly is the sole origin of the expansion anomaly which

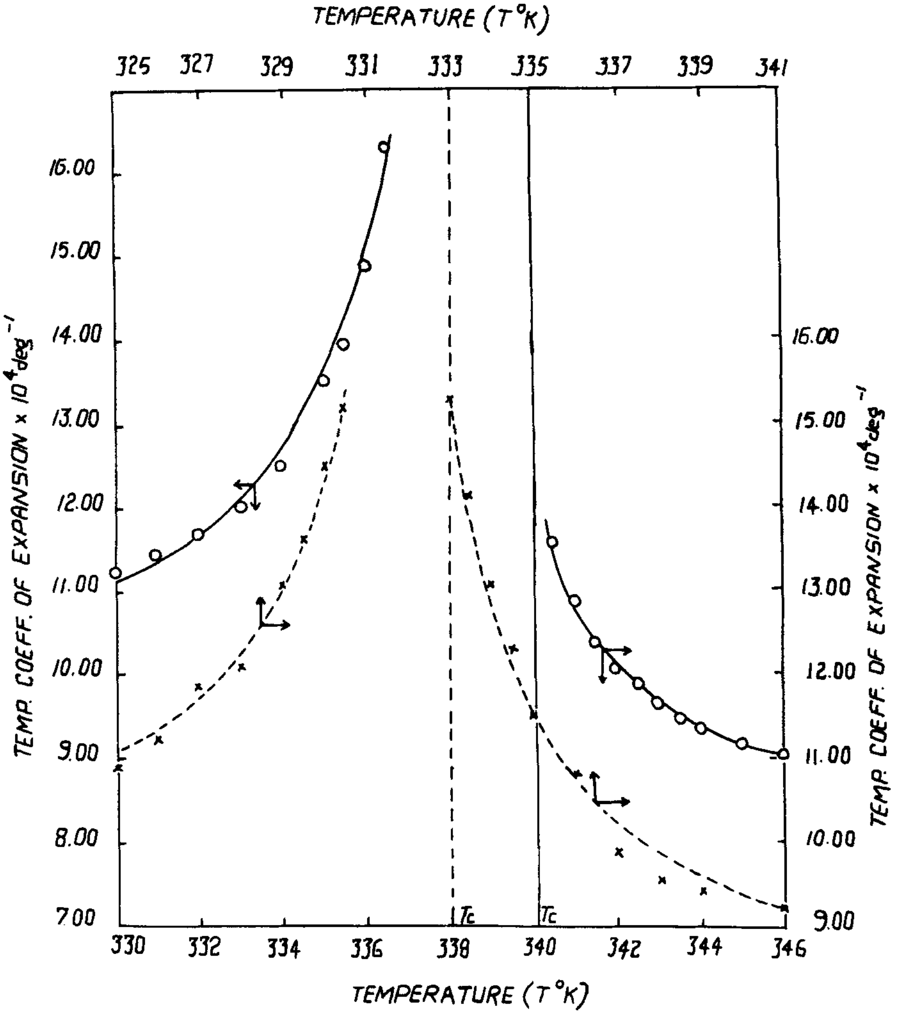

FIGURE 7 Experimental and theoretical values of α_T; (a) Mix. 2, experimental (○ ○ ○) and theoretical (————), (b) Mix. 3, experimental (× × ×) and theoretical (— — — —).

can be expressed as

$$\alpha_T = \alpha_0 + A(T - T^*)^{-\gamma} \tag{6}$$

From Eq. (5),

$$\frac{\mathrm{d}K_T}{\mathrm{d}T} = -\gamma C(T - T^*)^{-\gamma-1}$$

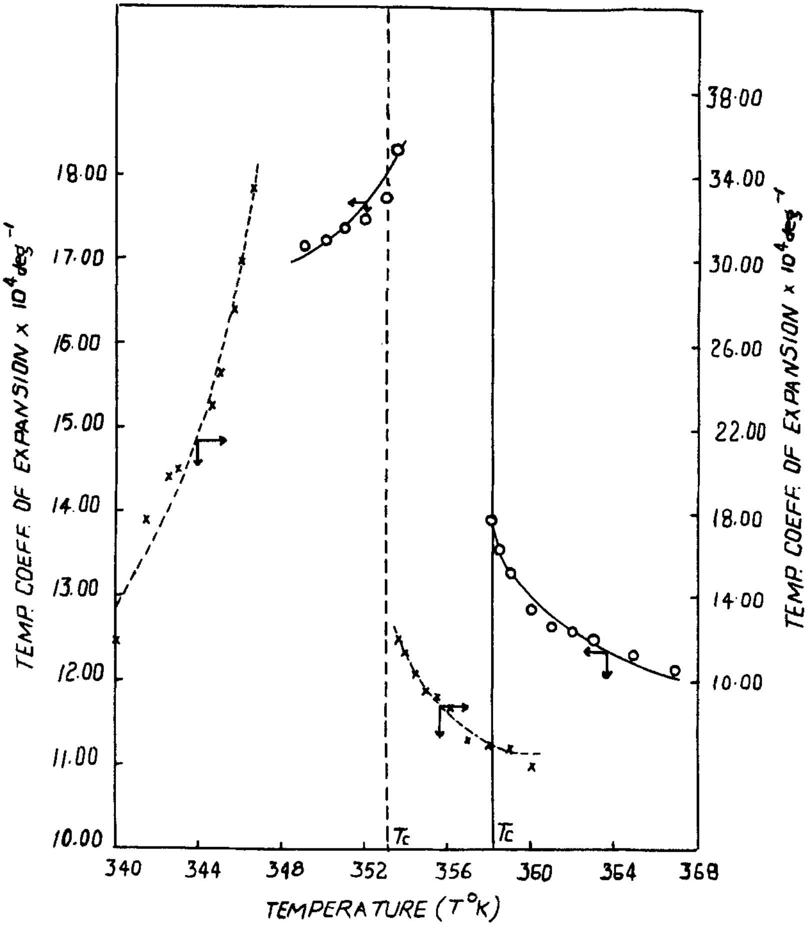

FIGURE 8 Experimental and theoretical values of α_T; (a) Mix. 5, experimental (O O O) and theoretical (————), (b) Mix. 6, experimental (× × ×) and theoretical (– – – –).

or

$$\frac{1}{K_T^0}\frac{\mathrm{d}K_T}{\mathrm{d}T} = C'(T - T^*)^{-\gamma-1} \tag{7}$$

where K_T^0 is taken at that temperature where the compressibility maximum occurs and C' is another constant. The relation between K_T and K_{ad} can be written as $K_T = \gamma \cdot K_{\mathrm{ad}}$, where γ is the ratio of specific heats. Since, the pre-transitional effects observed in K_T, C_p and α are similar in nature as that of K_{ad} and the ratio of specific heats as reported by earlier investigators,[14, 15] it can be reasonably assumed that the nature of variation of $1/K_{\mathrm{ad}}^0\,\mathrm{d}K_{\mathrm{ad}}/\mathrm{d}T$

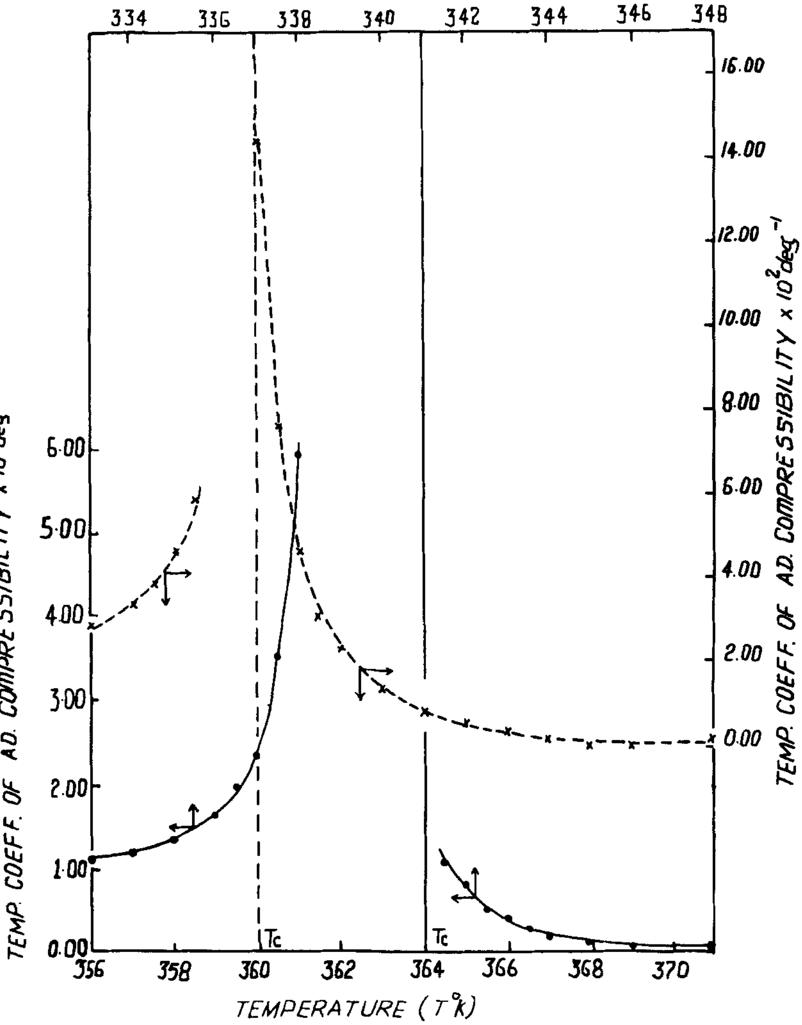

FIGURE 9 Experimental and theoretical values of β_T; (a) Mix. 1, experimental (× × ×) and theoretical (— — — —), (b) Mix. 4, experimental (● ● ●) and theoretical (————).

must be analogous to that of $1/K_T^\circ \, dK_T/dT$. Hence,

$$\frac{1}{K_T^\circ}\frac{dK_T}{dT} = -\,C'(T - T^*)^{-\gamma-1} \approx \frac{1}{K_{ad}^\circ}\frac{dK_{ad}}{dT}$$

or

$$\beta_T = \beta_0 + B(T - T^*)^{-\gamma'} \qquad (8)$$

TABLE II

Constants α_0, A and the critical exponent γ of thermal coefficient of expansion

Mixture No.		α_0	A	γ
Mix. 2	Nematic phase	0.245×10^{-2}	0.295×10^{-2}	0.99
	Isotropic phase	0.138×10^{-2}	0.128×10^{-2}	0.81
Mix. 3	Nematic phase	0.801	0.428	0.87
	Isotropic phase	0.106×10^{-2}	0.274×10^{-3}	0.72
Mix. 5	Nematic phase	-0.799×10^{-3}	0.160×10^{-2}	0.75
	Isotropic phase	0.789×10^{-3}	0.493×10^{-3}	0.72
Mix. 6	Nematic phase	0.856×10^{-3}	0.909×10^{-3}	0.66
	Isotropic phase	0.644×10^{-3}	0.926×10^{-3}	0.56

where $\beta_T = 1/K^{\circ}_{ad}\, dK_{ad}/dT$, β_0 is the constant away from transition free from fluctuations, B is a constant, T^* is the pseudocritical temperature and $\gamma' = \gamma + 1$.

Though Bendler's theory[13] and Landau-de Gennes theory[12] are expected to hold good only in the high temperature phase, Landau's original theory is expected to hold good on either side of the phase transition. Further, the nature of the pre-transitional effects observed on the low temperature side of the transition is similar to that of the high temperature side. Hence, the authors have tried to estimate the values of the critical exponents on either side of the nematic isotropic transition.

The results on the thermal coefficient of expansion and temperature coefficient of adiabatic compressibility have been fitted into Eqs. (6) and (8) by least square method and the results are presented in Tables II and III and Figures 7, 8 and 9. While applying Bendler's theory,[13] T^* was taken as $(T_C - 1)$ for nematic-isotropic transition.

The figures show good agreement between theoretical and experimental values. In thermal expansion curve, the critical exponents in the nematic phase are found in between 0.99 and 0.66 giving an average of 0.81. In the isotropic phase, the critical exponents are in between 0.81 and 0.56 giving an average of 0.70. These values of γ, which are close to unity are in agreement

TABLE III

Constants β_0, B and critical exponent γ' of temperature coefficient of adiabatic compressibility

Mixture No.		β_0	B	γ'
Mix. 1	Nematic phase	-0.511	0.961	1.81
	Isotropic phase	-0.354	0.148	1.58
Mix. 4	Nematic phase	0.103×10^{-1}	0.402	3.03
	Isotropic phase	-0.823×10^{-3}	0.215	1.40

with the value reported by de Gennes[12] for isotropic phase near nematic-isotropic transition.

For the temperature coefficient of compressibility, the critical exponents for the nematic phase are 1.81 and 3.03 for mixtures 1 and 4, respectively. In the isotropic phase, the corresponding values are 1.58 and 1.40 giving an average of 1.49. These values are closer to the expected value of 2.0 (since, γ' here is $\gamma + 1$).

A reasonable agreement between the theoretical and experimental values of the critical exponents could not be obtained, possibly due to the limitations of the temperature controlling device. The temperature control which varies within the limit of ±0.05°C and the temperature measurement that vary between ±0.01°C is perhaps not sufficient to study the behaviour very near to the phase transition. As such, we do not place much quantitative significance to the estimated value of γ. However, it is observed that γ has a tendency to decrease as the nematic ordering is decreased by the addition of the non-mesogenic compound (Table II). Further, the value of γ in the nematic phase side is always found to be higher than that of the corresponding isotropic phase side.

Acknowledgement

The authors are thankful to Professor R. V. Joshi and Professor S. M. Sen for their interest in the work. Thanks are also due to Mr. C. S. R. Murthy, Physical Research Laboratory, Ahmedabad for his help in computer calculations. Financial Assistance of the University Grants Commission is acknowledged.

References

1. S. Candau and S. V. Letcher, *Advances in Liquid Crystals*, Vol. 3, p. 168, Academic Press, New York (1978).
2. G. G. Natale, *Ultrasonics Symp. Proc., 366 (1977)*; *J. Acoust. Soc. Am.*, **63**, 1677 (1978).
3. C. G. Kartha, J. R. Otia, and A. R. K. L. Padmini, *Ind. J. Pure Appl. Phys.*, **12**, 648 (1974).
4. C. G. Kartha and A. R. K. L. Padmini, *Mol. Cryst. Liq. Cryst.*, **29**, 243 (1975).
5. J. R. Dyro and P. D. Edmonds, *Mol. Cryst. Liq. Cryst.*, **25**, 175 (1974).
6. S. Nagai, P. Martinoty, S. Candau, and R. Zana, *Mol. Cryst. Liq. Cryst.*, **31**, 243 (1975).
7. R. A. Vora and M. T. Chhangawala, Presented at the 7th International Liquid Crystal Conference, Bordex (1978).
8. G. W. Gray and B. Jones, *J. Chem. Soc.*, 1467 (1954).
9. K. S. Rao and B. R. Rao, *J. Scient. Ind.*, **16B**, 483 (1957).
10. J. R. Otia and A. R. K. L. Padmini, *Ind. J. Pure Appl. Phys.*, **11**, 190 (1973).
11. W. Maier and A. Saupe, *Z. Naturforsch*, **14(a)**, 882 (1959).
12. P. G. de Gennes, *Mol. Cryst. Liq. Cryst.*, **12**, 193 (1971).
13. J. Bendler, *Mol. Cryst. Liq. Cryst.*, **38**, 19 (1977).
14. A. Torgalkar, R. S. Porter, E. M. Barrall, and J. F. Johnson, *J. Chem. Phys.*, **48**, 3897 (1968).
15. C. G. Kartha, Ph.D. thesis, M. S. University of Baroda, Baroda (1972).