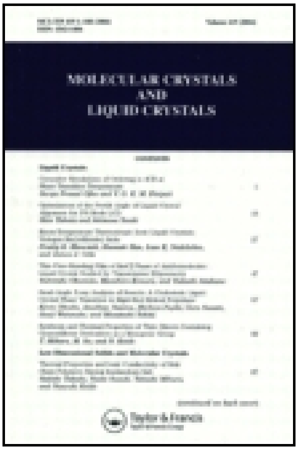

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

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Intermolecular Interactions in 4,4′-di-n-propoxy-azoxybenzene. Part II—Experimental

Nitish K. Sanyal [a] , R. A. Yadav [a] , S. R. Shukla [a] , Mihir Roychoudhury [a] & Durga Prasad Ojha [a]

[a] Department of Physics, University of Gorakhpur, Gorakhpur, 273 009, India

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Intermolecular Interactions in 4,4′-di-*n*-propoxy-azoxybenzene. Part II—Experimental

NITISH K. SANYAL, R. A. YADAV, S. R. SHUKLA, MIHIR ROYCHOUDHURY and DURGA PRASAD OJHA

Department of Physics, University of Gorakhpur, Gorakhpur - 273 009, India

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Temperature dependence of Ultrasonic velocity and specific volume have been studied in the case of 4,4′-di-*n*-propoxy-azoxybenzene dissolved in a non-interacting and non-mesogenic solvent, benzene, at different concentrations. The concentration of the liquid crystal molecules was chosen such that the intermolecular separation lies in the range of 8.5 Å to 13.5 Å. It was observed that the solutions of liquid crystalline substances exhibit interesting variations in the physical parameters as a function of temperatures. Physical quantities like adiabatic compressibility, molar sound velocity, molar compressibility and intermolecular freelength have also been calculated. Present study offers an experimental support to the probability distribution picture obtained with the help of our theoretical investigations.

Keywords: ultrasonic velocity, solution studies, molecular association, DPAB, phase transition, stacking interactions

INTRODUCTION

In an earlier paper of this series, a detailed analysis of theoretical investigations on the relative probabilities of various possible configurations of a pair of 4,4′-di-*n*-propoxy-azoxybenzene (DPAB) molecules was presented. It was observed that the molecules strongly prefer stacking interaction through a particular face referred to as S2. Other possible minimum energy configurations such as stacking through the other face S1 and in-plane interactions on both the sides of the molecules were also noticed. All the computations were carried out for an intermediate range of separation 6 Å to 8 Å. In order to confirm these theoretical findings, the liquid crystal were dissolved in a non-polar solvent Benzene at a concentration such that the intermolecular separation is close to the value at which the theoretical calculations were performed, and then to examine the behavior of this solution at different temperatures using techniques which could indicate the possible intermolecular associations. Since, the results obtained from theoretical calculations were corresponding to in vacuo interactions, the overall relative probabilities were recalculated for interactions in a dielectric medium. In the present paper, the results obtained from the measurement of ultrasonic velocity in the solution, the change in specific volume and other related parameters[1-7] at different temperatures have been reported along with the theoretical calculations mentioned above.

EXPERIMENTAL DETAILS

Liquid crystalline material 4,4′-di-*n*-propoxy-azoxybenzene procured from M/S Tokyo Kasie, Japan was dissolved as such without further purification in Benzene (AR) obtained from M/S BDH, India. Ultrasonic velocity was measured by a variable path interferometer (M/S Mittal Enterprises, New Delhi, India) having sensitivity ±0.1 meter/sec. at 2 MHz. Temperature regulation was achieved with the help of a thermostat U-10 (MLW, Germany) having accuracy of the order of ±0.1°C. The radiation correlation for temperature was also taken into consideration. Ultrasonic velocity was measured at different temperatures for the sample in the temperature range 37°C–72°C at concentrations 21%–5.25% by weight corresponding to intermolecular separation approximately 8.5 Å to 13.5 Å.

RESULTS AND DISCUSSION

The molecular geometry of DPAB molecule has been shown in Figure 1a and 1b with various atomic index numbers. Table I shows the relative probabilities of different minimum energy configurations calculated theoretically in vacuo and in a dielectric medium. The average dielectric constant of benzene has been taken as 2.25 for the entire temperature range. It may be observed that in dielectric medium, the probabilities are redistributed and there is a considerable rise in the probabilities of interactions, other than stacking through face S2, although the order of preference remains the same.

Figure 2 (Table II) shows the variation of ultrasonic velocity with

TABLE I

Relative probabilities of different minimum energy configurations in vacuo and in a dielectric medium average dielectric constant (Benzene) = 2.25

Configuration	Separation (Å)	E_{tot} (kcal/mole)	Probability (%) T = 300°K		Probability (%) T = 340°K		Probability (%) T = 396°K		Probability (%) T = 450°K	
			A*	B*	A*	B*	A*	B*	A*	B*
X(0°)Y(0°)	−6.0 (Z axis)	−3.8845	3.20	14.66	4.66	15.81	6.83	16.70	8.86	17.07
X(180°)Y(0°)	−6.0 (Z axis)	−5.9132	96.17	66.57	93.91	60.06	90.04	52.53	85.70	46.80
X(0°)Y(0°)	6.0 (Z axis)	−2.1959	0.19	4.16	0.38	5.20	0.80	6.43	1.34	7.37
X(180°)Y(0°)	6.0 (Z axis)	−2.3538	0.24	4.68	0.48	5.77	0.98	7.03	1.60	7.97
X(0°)	8.0 (Y axis)	−1.6114	0.07	2.69	0.16	3.54	0.38	4.62	0.70	5.51
X(180°)	8.0 (Y axis)	−1.7742	0.09	3.04	0.20	3.94	0.47	5.07	0.84	5.98
X(0°)	−8.0 (Y axis)	−1.4961	0.01	2.47	0.14	3.28	0.33	4.33	0.61	5.02
X(180°)	−8.0 (Y axis)	−1.0147	0.02	1.72	0.06	2.39	0.18	3.30	0.36	4.10

A* = Probability in vacuo
B* = Probability in a dielectric medium

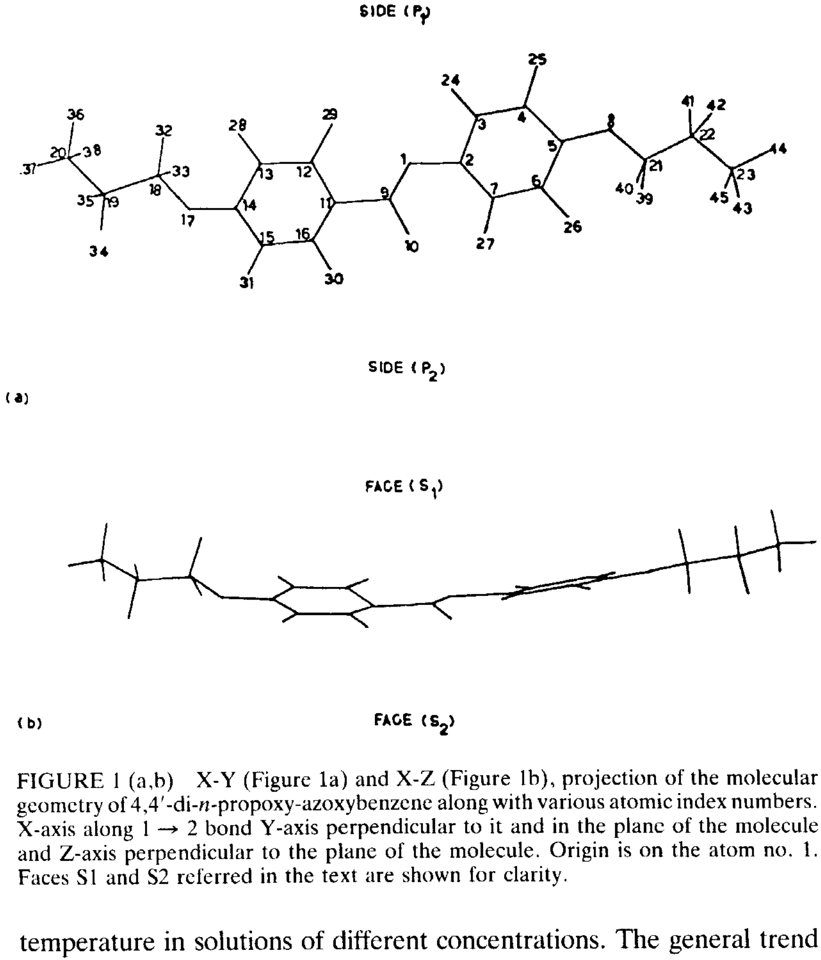

FIGURE 1 (a,b) X-Y (Figure 1a) and X-Z (Figure 1b), projection of the molecular geometry of 4,4′-di-*n*-propoxy-azoxybenzene along with various atomic index numbers. X-axis along 1 → 2 bond Y-axis perpendicular to it and in the plane of the molecule and Z-axis perpendicular to the plane of the molecule. Origin is on the atom no. 1. Faces S1 and S2 referred in the text are shown for clarity.

temperature in solutions of different concentrations. The general trend is that the velocity decreases with increasing temperature at all concentrations. At low concentration (5.25% corresponding to intermolecular separation 13.5 Å); the variation is analogous to an isotropic liquid showing steady decrease with increasing temperature.

For concentration 21% (corresponding to intermolecular separation 8.5 Å), some peculiarities are noticed as described below as the temperature is decreased up to 71.2°C, the velocity steadily increases with decreasing temperature. After 71.2°C, velocity decreases and attains a minimum at 70°C. There is a sharp rise in velocity in between 70°C–69.5°C which gradually decreases and then attains maxima at 68°C. Further decrease in temperature causes a minima in velocity at 67.5°C and the curve is linear in the lower regions. After sufficient

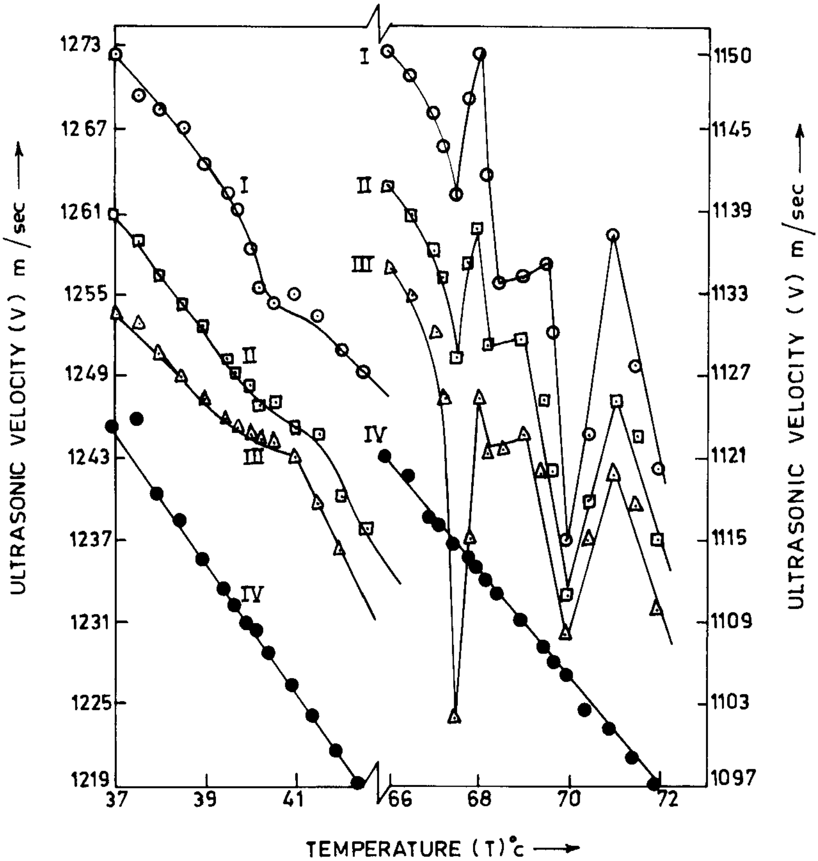

FIGURE 2 Temperature dependence of ultrasonic velocity (v) for 4,4′-di-*n*-propoxyazoxybenzene dissolved in benzene at 2 MHz.
I = 21g/100ml or $r \simeq 8.5$ Å
II = 14g/100ml or $r \simeq 9.5$ Å
III = 10.5g/100ml or $r \simeq 10.5$ Å
IV = 5.25g/100ml or $r \simeq 13.5$ Å

decrease in temperature, a small dip in the velocity curve is observed at about 40°C which again follows the usual pattern at lower temperatures. It may also be noticed from Figure 2 (Curve I, II, III) that the minima at 67.5°C are less pronounced at higher concentrations of the solute molecules while the minima corresponding to 70°C, shows an opposite behavior.

Figure 3 (Table III) shows the variation of specific volume with respect to temperature at particular concentrations. A change in slope is observed at 68.5°C–69.5°C and near 40°C–42°C. Derived param-

TABLE II

Variation of ultrasonic velocity with temperature in the solution of 4,4′-di-*n*-propoxy-azoxybenzene and benzene at different concentrations

Temperature (T)°C	Ultrasonic velocity (V) m/s I 21g/100ml	II 14g/100ml	III 10.50g/100ml	IV 5.25g/100ml
37.0	1272.0	1260.5	1253.5	1245.0
37.5	1270.0	1258.5	1252.0	1245.5
38.0	1268.0	1256.0	1250.0	1240.0
38.5	1266.5	1254.0	1248.5	1238.0
39.0	1264.5	1252.0	1247.0	1235.5
39.5	1262.0	1250.0	1245.5	1233.0
39.7	1261.0	1249.0	1245.0	1232.0
40.0	1258.5	1248.0	1244.5	1230.5
40.2	1255.0	1247.0	1244.0	1230.0
40.5	1254.0	1247.0	1244.0	1228.5
41.0	1254.5	1245.0	1243.0	1226.0
41.5	1253.0	1244.5	1239.5	1223.5
42.0	1250.5	1240.0	1236.0	1221.5
42.5	1249.0	1237.5	1232.5	1219.0
66.0	1150.0	1140.5	1134.5	1121.0
66.5	1148.0	1138.5	1132.5	1119.0
67.0	1146.0	1136.0	1130.0	1116.5
67.2	1143.5	1134.0	1125.0	1116.0
67.5	1140.0	1128.0	1102.0	1114.5
67.8	1147.0	1135.0	1115.0	1113.5
68.0	1150.0	1137.5	1125.0	1113.0
68.2	1141.5	1129.0	1121.0	1112.0
68.5	1133.5	1129.0	1121.5	1111.0
69.0	1134.0	1129.0	1122.5	1109.0
69.5	1135.0	1125.0	1120.0	1107.0
69.7	1130.0	1120.0	1115.0	1106.0
70.0	1115.0	1111.0	1108.0	1105.0
70.5	1122.5	1117.5	1115.0	1102.5
71.0	1137.0	1125.0	1120.0	1101.0
71.5	1127.5	1122.5	1117.5	1099.0
72.0	1120.0	1115.0	1110.0	1097.0

eters such as adiabatic compressibility, molar sound velocity and intermolecular free lengths have been plotted against temperature for the same concentration *i.e.* 21% solution (intermolecular separation equal to 8.5 Å) and shown in Figures 4 and 5 (Table III).

On the basis of the results of theoretical investigations, the nature of the experimental curves may be explained as follows:

At very low concentration (say 5.25%, curve IV in the Figure 2), since intermolecular distances are large, the interactions between the solute molecules are extremely weak. The solution, therefore shows the characteristics similar to those of an isotropic liquid. The observed

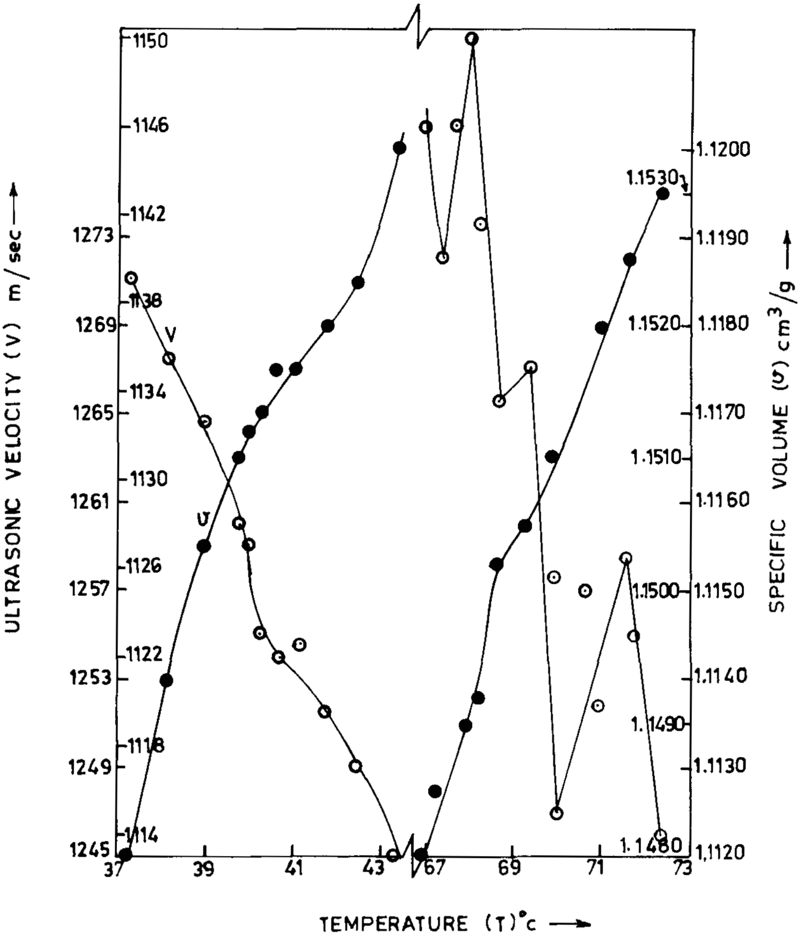

FIGURE 3 Temperature dependence of ultrasonic velocity (V) and specific volume (v) for solution I.

steady decrease in ultrasonic velocity with increasing temperature, confirms this proposition. Also, it will be reasonable to think that the observed variations in the solutions of higher concentrations (more than 10%), is due to increased solute–solute interactions and consequent decrease in solute–solvent interactions.

At high temperatures, when the thermal agitations are strong enough, intermolecular interactions have relatively minor effects and hence the behavior of the solution is expected to be similar to that of an isotropic liquid. Therefore, for temperatures beyond 72°C, at all concentrations, no anomalous (rise or fall) in ultrasonic velocity, specific

TABLE III

Variation of physical parameters in the solution of 4,4′-di-*n*-propoxy-azoxybenzene and benzene at concentration 21g/100ml

Temperature (T)°C	Velocity (V) m/s	Specific volume (v) cm^3/g	Ad. compressibility (β ad) 10^{12}cm^2/dyne	Molar sound velocity (R) cm^3 (m/s)$^{1/3}$	Molar compressibility (B) cm^3 (dyne/cm^3)$^{1/7}$	Intermolecular free length (L$_f$) A.U.
37.3	1271.0	1.1120	68.83	3787	190.99	0.5235
38.2	1267.5	1.1140	69.34	3790	191.13	0.5254
39.0	1264.5	1.1155	69.76	3792	191.22	0.5270
39.8	1260.0	1.1165	70.33	3791	191.19	0.5291
40.0	1259.0	1.1168	70.46	3791	191.19	0.5297
40.3	1255.0	1.1170	70.92	3788	191.05	0.5314
40.7	1254.0	1.1175	71.07	3789	191.08	0.5319
41.1	1254.5	1.1175	71.01	3789	191.01	0.5317
41.8	1251.5	1.1180	71.38	3788	191.04	0.5331
42.5	1249.0	1.1185	71.70	3787	191.01	0.5343
43.4	1245.0	1.1200	72.26	3788	191.05	0.5364
67.0	1146.0	1.1480	87.41	3777	190.56	0.5899
67.4	1140.0	1.1485	88.37	3772	190.35	0.5931
67.7	1146.0	1.1485	87.45	3778	190.64	0.5901
68.0	1150.0	1.1490	86.88	3785	190.90	0.5881
68.2	1141.5	1.1492	88.20	3776	190.53	0.5926
68.7	1133.5	1.1502	89.52	3771	191.21	0.5970
69.4	1135.0	1.1505	89.31	3773	191.39	0.5963
69.9	1225.0	1.1510	90.86	3764	190.01	0.6015
70.1	1115.0	1.1511	92.59	3753	189.52	0.6072
70.6	1125.0	1.1515	90.98	3765	190.06	0.6019
71.0	1137.0	1.1520	89.12	3780	190.71	0.5957
71.6	1126.5	1.1525	90.82	3770	190.26	0.6013
71.8	1123.0	1.1525	91.38	3766	190.09	0.6032
72.4	1114.0	1.1530	92.91	3757	189.73	0.6082

volume or in any of the related parameters is observed. Theoretical investigations show maximum probability (60% at 340°K) for stacking interactions through face S2 (see Figure 1b for definition of face S2) with X(180°)Y(0°). Also, on rotating the molecule about X-axis at relatively large separation (8 Å or higher), the energy minimum occurs at 270° which shifts to X(180°)Y(0°) configuration at a closer separation (3.4 Å). Thus in solution, on reducing temperature from 71°C, the initial stacking seems to be taking place between the molecules at X(270°)Y(0°) for one molecule and S2 face for the other. Initially there is stacking between the molecules which gets completed when the temperature is lowered to 70°C. On further lowering, the ultrasonic velocity again rises for about 1°C. Up to this temperature range, the slope of the specific volume is constant since such asso-

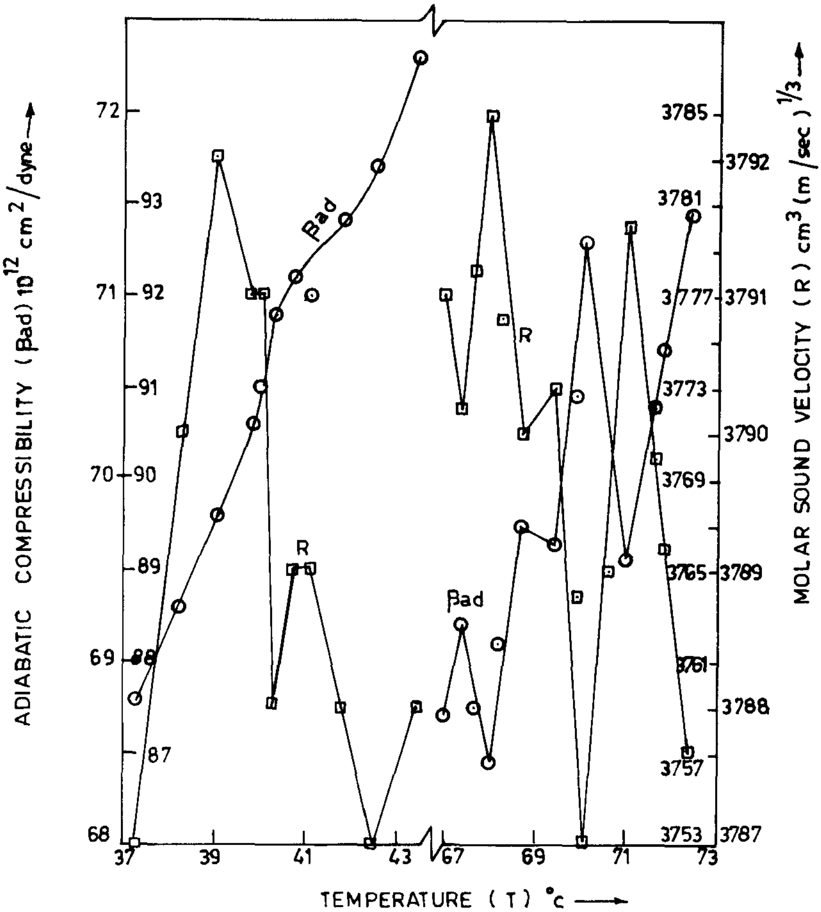

FIGURE 4 Temperature dependence of adiabatic compressibility (βad) and molar sound velocity (R) for solution I.

ciations do not produce any cavity inside the material bulk. Molar sound velocity also shows the same trend as ultrasonic velocity while the adiabatic compressibility curve shows that the solution becomes more compressible in the temperature range 71°C to 70°C and then regains its original characteristic *i.e.* reduction of compressibility with decrease temperature. Also, between 71°C–70°C, intermolecular free length increases indicating association of molecules and thus reduction in the number of independent units in the solution. On further lowering of temperature from about 69.5°C to 68.3 ± 0.02°C, the small decrease in ultrasonic velocity, molar sound velocity and slight increase in adiabatic compressibility and intermolecular free length,

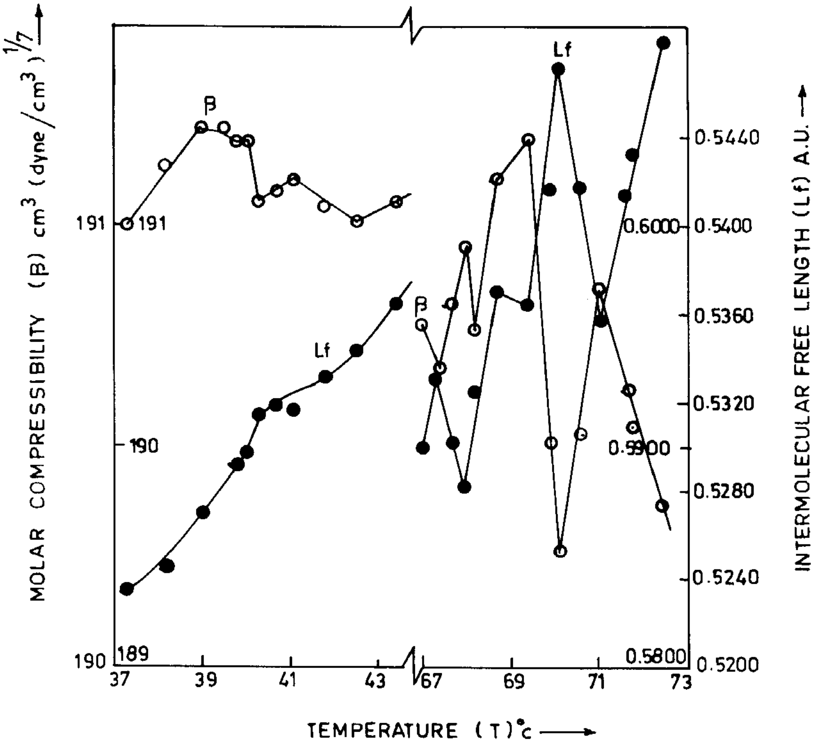

FIGURE 5 Temperature dependence of molar compressibility (B) and intermolecular freelength (L_f) for solution I.

suggest that in this range no new association takes place but an adjustment in the earlier association scheme is probable. Thus, it may be correlated with the theoretically predicted X(270°)Y(0°) → X(180°)Y(0°) adjustment in the stacking pattern through S2 surfaces of the solute molecules.[8,9]

It is interesting to note that, as in this region stacking is perfect and the solvent molecules are pushed out from the regions between the stacked molecules, a pseudo increase in the total volume may be visualized. The observed alternation in the rate of change in specific volume in the region gives a further support to this.

On further lowering of temperature up to 68°C, the normal trend is observed but for the temperature range 68°C–67.5°C, again a fall in the ultrasonic velocity and corresponding changes in other parameters are observed. This behavior can be correlated with in-plane interactions between the sides of the molecules. Below 67.5°C and for a considerable range of temperature there is no unusual variation in the plot shown and at close to 40°C, a small dip in the ultrasonic velocity and corresponding change in other parameters are observed. In this region, the change in the rate of decrease of specific volume indicates that there is a likelihood of secondary stacking due to rearrangement of stacked pairs. Thus, one may correlate[10,11] this with interactions between stacked pairs either through a further non-specific stacking or terminal interaction. The insignificant changes observed in adiabatic compressibility and intermolecular free length supports this proposition.

CONCLUSION

The present paper offers an experimental support to the probability distribution picture obtained with the help of our theoretical calculations. Also, this provides a new and interesting way of looking at the liquid crystalline molecules in the solutions.

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