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Behaviour of Ultrasonic Velocity in Cholesteric Liquid Crystals

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Ultrasonic velocities (V) have been determined, employing a fixed path double crystal interferometer, in three cholesteric liquid crystals, namely cholesteryl propionate, cholesteryl laurate and cholesteryl myristate in their isotropic and anisotropic phases including the region of the phase transition. The variation of specific volume (v) is also studied in the same temperature range by a special dilatometer constructed for this purpose. Anomalous behaviour of ultrasonic velocity is observed near the isotropic-cholesteric phase transition in all three compounds. In the two polymesomorphic liquid crystals, namely cholesteryl laurate and cholesteryl myristate, contrary to the ultrasonic behaviour of cholesteryl stearate, prominent velocity dips are observed at cholesteric-smectic transition temperatures. The parameters adiabatic compressibility (β_{ad}) and molar sound velocity (R) are estimated and they are found to exhibit sudden jumps at cholesteric-smectic and isotropic-cholesteric transitions. The thermal expansion and temperature co-efficient of compressibility are found to show abnormal increase near the phase transition indicating the existence of large-magnitude pre-transitional effects near the phase transition. A comparative study of the ultrasonic behaviour of six aliphatic esters of cholesterol has shown that the magnitude of the velocity dip observed at the isotropic-cholesteric transition increased with increase of molecular weight and only cholesteryl acetate shows deviation.

INTRODUCTION

Considerable interest has been shown recently for the study of liquid crystals near their isotropic-anisotropic phase transition as they are found to exhibit anomalies in a number of physical properties. Liquid crystals are generally classified into three types—smectic, nematic and cholesteric depending on their internal molecular structure. Among these liquid crystals, the cholesteric phase is considered as a special case of the nematic phase; in the former the axes of the molecules are themselves optically active, unlike the latter. In the cholesteric phase the molecular structure corresponds to a twisted nematic layer having parallel orientation of the molecules along their long axes, and superimposed on the parallel orientation there is a spontaneous and continuous twist. The smectic phase is characterised by layered structure and in each layer the molecules are arrayed parallel to one another with their long axes perpendicular to the smectic plane, however the spacing of the molecules in each layer is not the same.

Anomalies in a number of physical properties such as specific volume, viscosity, surface tension, and specific heat have been reported near the mesophase-isotropic transition of some cholesteric and nematic types of liquid crystals by a number of workers.[1–5] Gabrielli and Verdini[6] were the first to investigate ultrasonic velocity and absorption in *p*-azoxyanisole, and reported anomalies at the isotropic-nematic phase transition. Later Hoyer and Nolle[4] and Kapustin and Bykova[7] have studied ultrasonic properties of *p*-azoxyanisole and *p*-*n*-octyloxybenzoicacid, *p*-*n*-heptyloxybenzoicacid respectively, and they have reported anomalies near the isotropic-mesophase transitions of these liquid crystals. Kartha and Padmini[8] have investigated the ultrasonic velocity and absorption in some cholesteric liquid crystals while Otia and Padmini[9] have studied ultrasonic velocity and other parameters in MBBA. They have reported abrupt jumps in velocity, specific volume and other parameters in all the liquid crystals studied.

In view of the interesting and anomalous properties exhibited by the liquid crystals near their isotropic-mesophase transition and in view of the little work done on ultrasonic properties of liquid crystals, three cholesteric liquid crystals, cholesteryl propionate, cholesteryl laurate and cholesteryl myristate were chosen for investigating systematically the ultrasonic velocity, density and other related parameters throughout their mesophase and 10 to 15°C beyond the isotropic-mesophase transition. Among these three liquid crystals cholesteryl propionate exhibits only the cholesteric phase while cholesteryl laurate and cholesteryl myristate exhibit both smectic and cholesteric phases.

EXPERIMENTAL DETAILS AND PROCEDURE

The velocity measurements are done by a fixed path double crystal interferometer.[10] It consists of two X-cut quartz discs of 1 in. diameter and fundamental frequency 2 MHz fixed on the opposite faces of a stainless steel cell which contains the liquid crystal. The R.F. voltage from a variable frequency oscillator is taken out through a shielded cable and is applied to one of the two quartz crystals. The received voltage across the second crystal is communicated to a sensitive A.C. vacuum tube voltmeter, which acts as a wide band amplifier enabling direct measurements up to 0.1 millivolt.

The oscillator frequency is varied and a position is set at which the V.T.V.M. reads a maximum for which position the oscillator frequency is accurately measured by a BC-221 frequency meter. The frequency is continuoulsy varied to cover 10 maxima and the frequency is again measured. This is repeated to cover about 100 maxima and the mean value of Δf is estimated. By substituting the value of Δf and the distance between the two crystals L in the following relation, velocity V is calculated

$$V = 2L \times \Delta f$$

The parallelism between the inner faces of two crystals must be of a very high order so as to enable maxima in V.T.V.M. to occur very sharply. This is achieved by machining the two opposite surfaces of the cell on a precision milling machine. It is found that boundary effects do not play any part in vitiating the results since the size of the liquid column (3 cms) is large compared to the width of the sound beam, the frequency is high enough to neglect the diffraction effects due to the spreading of the sound beam. The measurements are taken away from the resonance frequency of the crystal least the pulling effect of the crystal vitiates the results.

The interferometer cell is immersed in the oil bath so as to reach the level a little below the lid of the cell and the temperature of the bath is controlled to 0.05°C by using a nitrobenzene-mercury-in-glass thermostat along with an electronic relay, and the temperatures are measured to an accuracy of 0.05°C by a chromel-alumel thermocouple. In order to avoid any oxidation of the substance, nitrogen gas which is free from oxygen and moisture is passed through the cell during the course of the measurements. The velocities are measured at a frequency of 2 MHz and they are accurate to 1 m/sec. The densities are measured by a special dilatometer. The densities estimated are accurate to 0.0001 g/cm^3.

The cholesteryl myristate and laurate are obtained from M/s. Aldrich Chemical Company, Inc., U.S.A. and cholesteryl propionate from M/s. Koch–Light Laboratories Limited, U.K. These chemicals are dissolved in alcohol and recrystallized, and the transition temperatures are measured by using a polaroid arrangement. The transition temperatures obtained are 112°C (T_c) for propionate, 84°C (T_c) and 79°C (T_s) for myristate and 88°C (T_c) and 80.8°C (T_s) for laurate.

PRESENTATION OF RESULTS

The ultrasonic velocities (V) and densities (ρ) are measured in all the three liquid crystals throughout their anisotropic region and 10° to 15°C beyond the phase transition. Special attention has been paid near the cholesteric-smectic and the isotropic-cholesteric phase transitions of cholesteryl myristate and laurate while in cholesteryl propionate, only near the isotropic-cholesteric phase transition.

The ultrasonic velocities are reported for the first time in all the three compounds. The parameters adiabatic compressibility (β_{ad}), molar sound velocity (R) and molar compressibility (B) are estimated from the following relations:

$$\beta_{ad} = (1/\rho V^2),\ R = \frac{M}{\rho}(V)^{1/3} \quad \text{and} \quad B = \frac{M}{\rho}(\beta_{ad})^{-1/7}$$

where V, ρ and M are the ultrasonic velocity, the density and the molecular weight respectively. The results of V, v, β_{ad}, R and B are presented in Tables I, II and III and the results of V, v and β_{ad} are plotted in Figures 1, 2, 3, and 4.

The values of thermal expansion co-efficient $\alpha_v = [(1/v_0)(\mathrm{d}v/\mathrm{d}t)]$ and temperature co-efficient of adiabatic compressibility $\alpha_\beta = (1/\beta_0)(\mathrm{d}\beta/\mathrm{d}t)$ are also estimated near the isotropic-cholesteric and the cholesteric-smectic transition and the results are plotted in Figures 5, 6 and 7.

TABLE I

Values of velocity, specific volume, adiabatic compressibility, molar sound velocity and molar compressibility for cholesteryl myristate.

Temp. °C t	Velocity m/sec V	Specific volume cm^3/g v	Adiabatic compressibility cm^2/dyne $\beta_{ad} \times 10^{12}$	Molar sound velocity R	Molar compressibility B
72.0	1390	0.7843	40.60	5226	275.8
73.0	1386	0.7855	40.88	5226	275.8
74.2	1382	0.7870	41.21	5234	276.3
75.2	1377	0.7882	41.53	5234	276.3
76.2	1373	0.7894	41.86	5237	276.4
77.4	1367	0.7910	42.35	5241	276.5
78.0	1358	0.7918	42.94	5237	276.2
78.4	1336	0.7922	44.39	5207	275.1
79.0	1318	0.7936	45.69	5193	274.5
79.4	1340	0.7940	44.24	5224	275.8
79.8	1351	0.7944	43.51	5242	276.9
80.8	1358	0.7953	43.12	5257	277.3
82.0	1357	0.7964	43.21	5264	277.6
82.7	1353	0.7971	43.56	5262	277.5
83.2	1346	0.7976	44.02	5257	277.3
83.6	1304	0.7980	46.94	5205	274.9
84.0	1345	0.7989	44.13	5260	277.6
85.4	1336	0.7998	44.82	5258	277.3
86.0	1333	0.8002	45.05	5257	277.3
88.0	1324	0.8015	45.70	5254	277.2
90.0	1316	0.8026	46.36	5249	277.0
92.0	1310	0.8038	46.87	5250	277.0
94.6	1293	0.8054	48.14	5237	276.5

TABLE II

Values of velocity, specific volume, adiabatic compressibility, molar sound velocity and molar compressibility for cholesteryl laurate

Temp. °C t	Velocity m/sec V	Specific volume cm^3/g v	Adiabatic compressibility cm^2/dyne $\beta_{ad} \times 10^{12}$	Molar sound velocity R	Molar compressibility B
73.0	1384	1.1125	58.10	7053	354.3
75.0	1379	1.1152	58.66	7062	354.6
77.0	1370	1.1176	59.56	7063	354.6
79.0	1361	1.1205	60.52	7065	354.8
80.0	1344	1.1222	62.16	7046	353.9
80.7	1332	1.1229	63.29	7030	353.3
81.4	1359	1.1235	60.81	7081	355.5
82.0	1356	1.1242	61.17	7074	355.4
84.0	1342	1.1263	62.56	7068	355.0
85.4	1334	1.1279	63.40	7065	354.8
87.0	1318	1.1304	65.10	7050	354.2
87.6	1310	1.1313	65.90	7044	353.9
88.0	1298	1.1321	67.20	7028	353.2
88.5	1314	1.1326	65.61	7058	354.5
89.0	1317	1.1330	65.29	7066	354.9
89.2	1312	1.1330	65.83	7057	354.4
90.5	1294	1.1340	67.77	7031	353.3
92.2	1284	1.1354	68.87	7021	352.9
95.2	1278	1.1379	69.69	7021	352.9
97.0	1272	1.1392	70.41	7023	353.0
98.5	1268	1.1402	70.93	7023	353.0

DISCUSSION

A study of the Figures 1, 2 and 3 reveals that the ultrasonic velocity exhibits anomalous behaviour in all these three compounds near phase transitions. In the case of propionate the ultrasonic velocity is found to show abrupt minimum while in cholesteryl laurate which exhibits two transition temperatures T_c and T_s characterising the isotropic-cholesteric and the cholesteric-smectic transitions, the velocity shows abrupt drop at both the transitions; though the dip observed at the cholesteric-smectic transition is larger than the dip at the isotropic-cholesteric transition. A study of the ultrasonic velocity in cholesteryl myristate indicates that it exhibits analogous behaviour to that of laurate in showing velocity minimum at the isotropic-cholesteric and cholesteric-smectic phase transitions. This interesting observation is contrary to the observation made by Zvereva and Kapustin[11]

TABLE III

Values of velocity, specific volume, adiabatic compressibility, molar sound velocity and molar compressibility for cholesteryl propionate

Temp. °C t	Velocity m/sec V	Specific volume cm^3/g v	Adiabatic compressibility cm^2/dyne $\beta_{ad} \times 10^{12}$	Molar sound velocity R	Molar compressibility B
100.0	1268	1.0958	68.13	5250	265.5
102.0	1265	1.0973	68.50	5255	265.6
104.4	1261	1.0993	69.16	5257	265.7
106.0	1257	1.1004	69.64	5258	265.8
107.2	1254	1.1014	70.08	5258	265.7
108.0	1251	1.1020	70.36	5258	265.7
109.4	1246	1.1031	71.04	5254	265.6
110.2	1242	1.1037	71.56	5252	265.5
111.0	1239	1.1043	71.88	5250	265.5
111.5	1220	1.1050	74.25	5228	264.4
112.0	1210	1.1057	75.47	5216	263.9
112.5	1228	1.1065	73.38	5244	265.2
112.7	1235	1.1068	72.59	5255	265.7
113.2	1230	1.1072	73.21	5252	265.5
114.5	1226	1.1081	73.72	5250	265.5
115.6	1220	1.1089	74.51	5246	265.3
117.4	1217	1.1102	74.90	5247	265.3
120.2	1212	1.1123	75.72	5250	265.5
122.0	1208	1.1137	76.31	5250	265.5
124.4	1204	1.1154	76.94	5253	265.6

who investigated cholesteryl caprinate which is also a polymesomorphic crystal exhibiting cholesteric and smectic phases; they have not observed any abrupt drop in velocity at the cholesteric-smectic transition. Kartha and Padmini[8] also have not observed any anomaly near the cholesteric-smectic transition of another polymesomorphic crystal, cholesteryl stearate. Kapustin and Bykova[7] have observed in *p*-*n*-octyloxy benzoic acid and *p*-*n*-heptyloxy benzoic acid only a slight change in slope of the velocity-temperature curve, at the smectic-nematic transitions, but a sharp decrease in velocity at the isotropic-nematic transition.

The specific volume exhibits a remarkable linear variation in both the isotropic and anisotropic regions in all the three liquid crystals. The cholesteryl propionate shows a volume jump of 0.0028 at T_c, while cholesteryl myristate 0.0010 at T_c and 0.0013 at T_s, and cholesteryl laurate 0.0034 at T_c and 0.0017 at T_s respectively.

A glance at the temperature variation of adiabatic compressibility in these

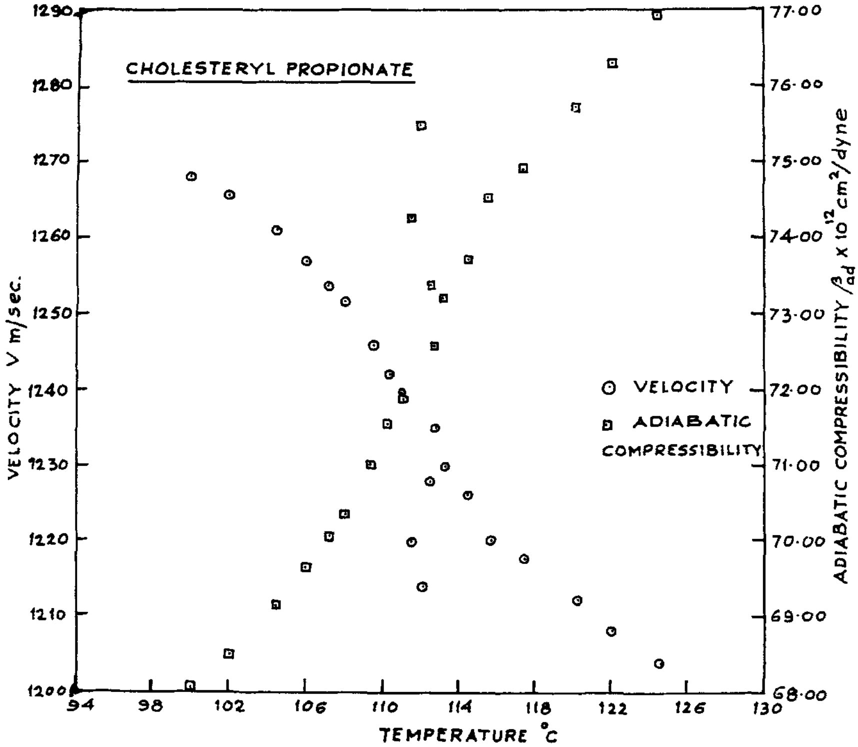


FIGURE 1 Temperature variation of ultrasonic velocity (V) and adiabatic compressibility (β_{ad}) in cholesteryl propionate.

compounds shows that though the velocity is not linear in isotropic and anisotropic phases of cholesteryl propionate, the adiabatic compressibility exhibits good linearity in both the phases far away from the transition, while at transition it shows a sudden jump. This behaviour is similar to the behaviour exhibited by other liquid crystals—namely, cholesteryl formate, cholesteryl acetate and cholesteryl benzoate. In cholesteryl myristate the adiabatic compressibility is quite linear in the isotropic phase, while it is nearly linear in the anisotropic phase; it exhibits abrupt jump in its value at both the isotropic-cholesteric and the cholesteric-smectic transitions. In the case of cholesteryl laurate, β_{ad} exhibits abrupt changes near the transition T_c and T_s while it is non-linear in both the isotropic and the anisotropic regions.

A study of the molar sound velocity shows that it exhibits abrupt drop in its value near each phase transition of every liquid crystal. In the case of cholesteryl propionate the drop is about 39 while in the case of laurate and myristate

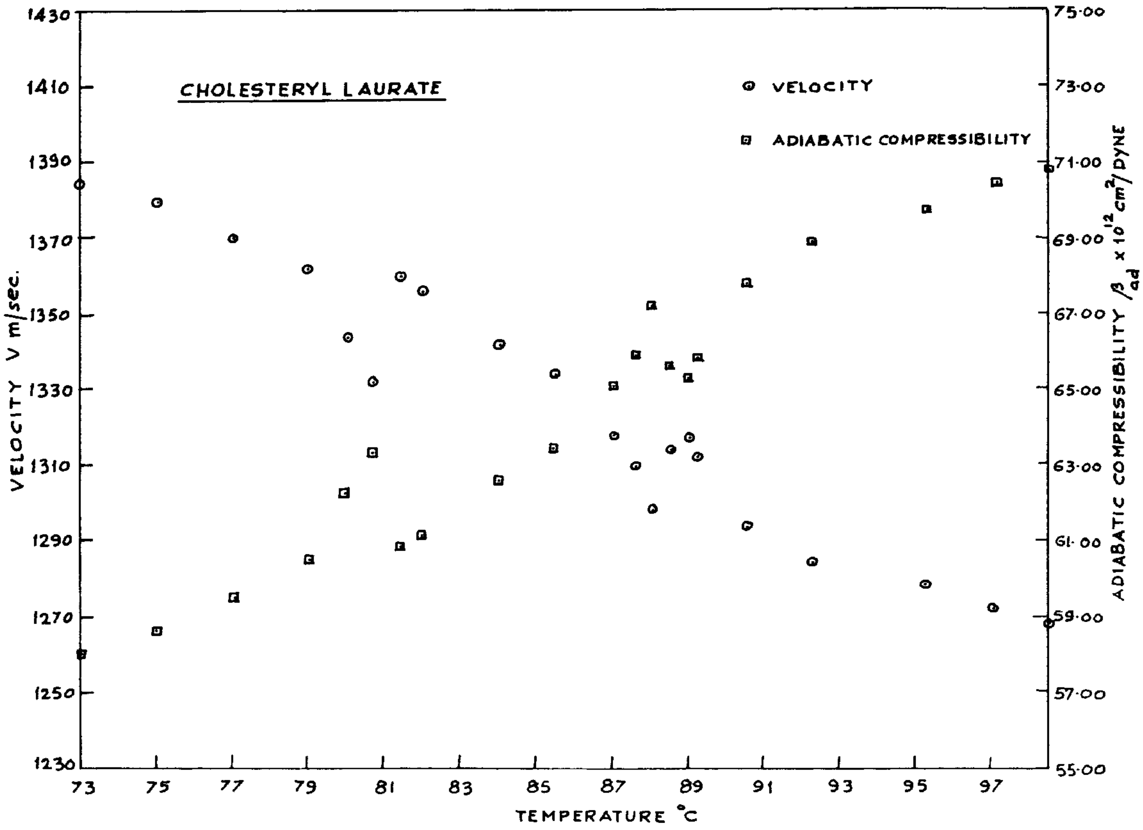


FIGURE 2 Temperature variation of ultrasonic velocity (V) and adiabatic compressibility (β_{ad}) in cholesteryl laurate.

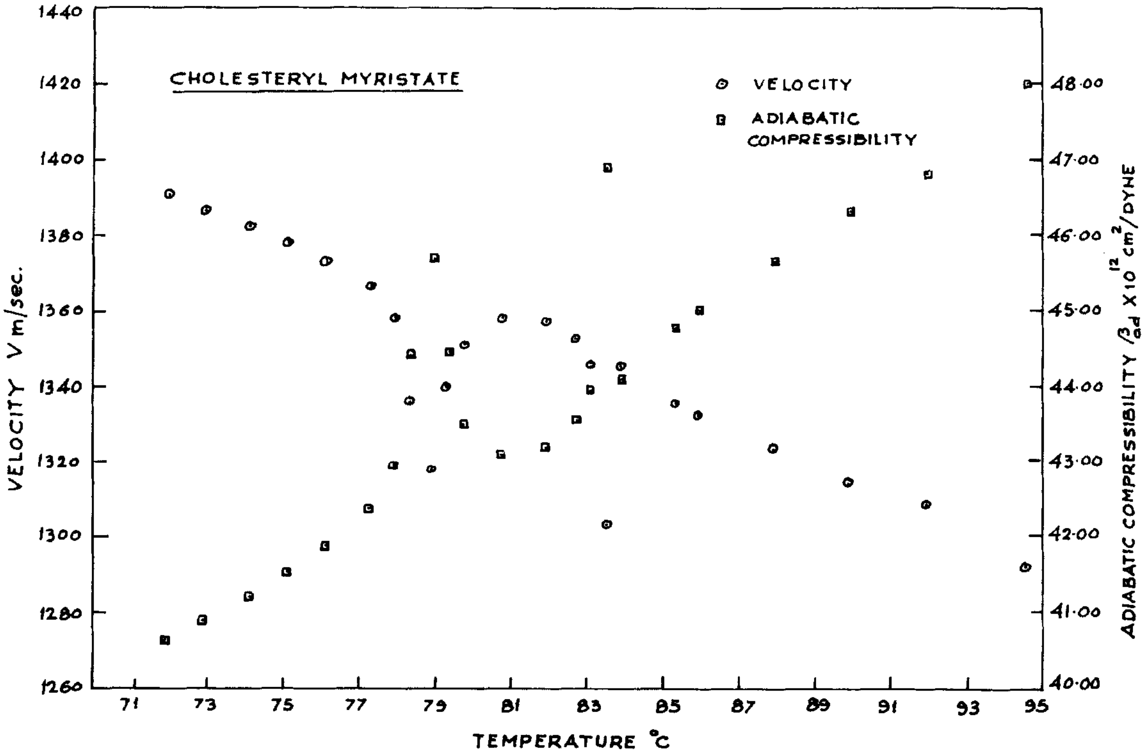
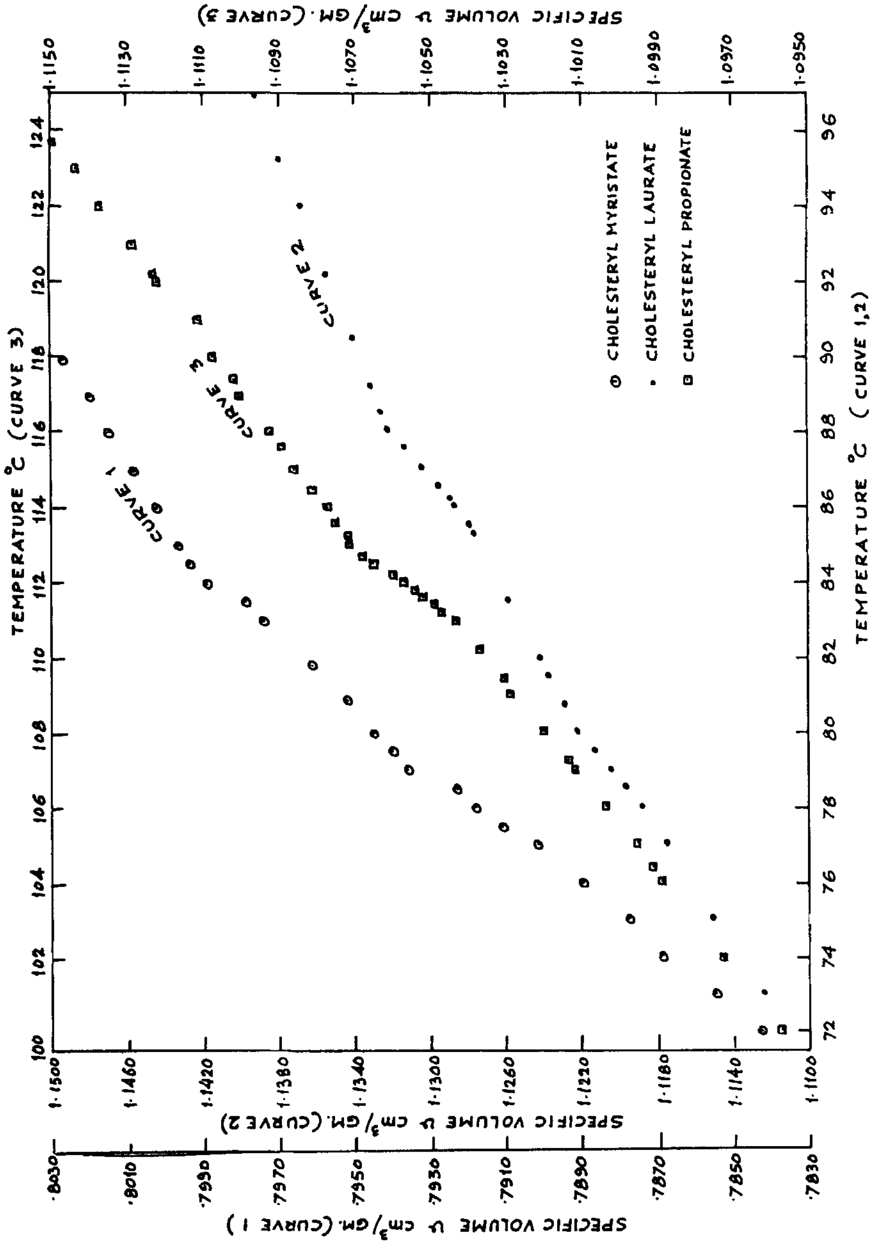


FIGURE 3 Temperature variation of ultrasonic velocity (V) and adiabatic compressibility (β_{ad}) in cholesteryl myristate.


SPECIFIC VOLUME υ cm³/GM. (CURVE 3)
1.1150
1.1130
1.1110
1.1090
1.1070
1.1050
1.1030
1.1010
1.0990
1.0970
1.0950
TEMPERATURE °C (CURVE 3)
100
102
104
106
108
110
112
114
116
118
120
122
124
TEMPERATURE °C (CURVE 1,2)
72
74
76
78
80
82
84
86
88
90
92
94
96
SPECIFIC VOLUME υ cm³/GM. (CURVE 2)
1.1500
1.1460
1.1420
1.1380
1.1340
1.1300
1.1260
1.1220
1.1180
1.1140
1.1100
SPECIFIC VOLUME υ cm³/GM. (CURVE 1)
·8030
·8010
·7990
·7970
·7950
·7930
·7910
·7890
·7870
·7850
·7830
CURVE 1
CURVE 2
CURVE 3
⊖ CHOLESTERYL MYRISTATE
• CHOLESTERYL LAURATE
⊡ CHOLESTERYL PROPIONATE

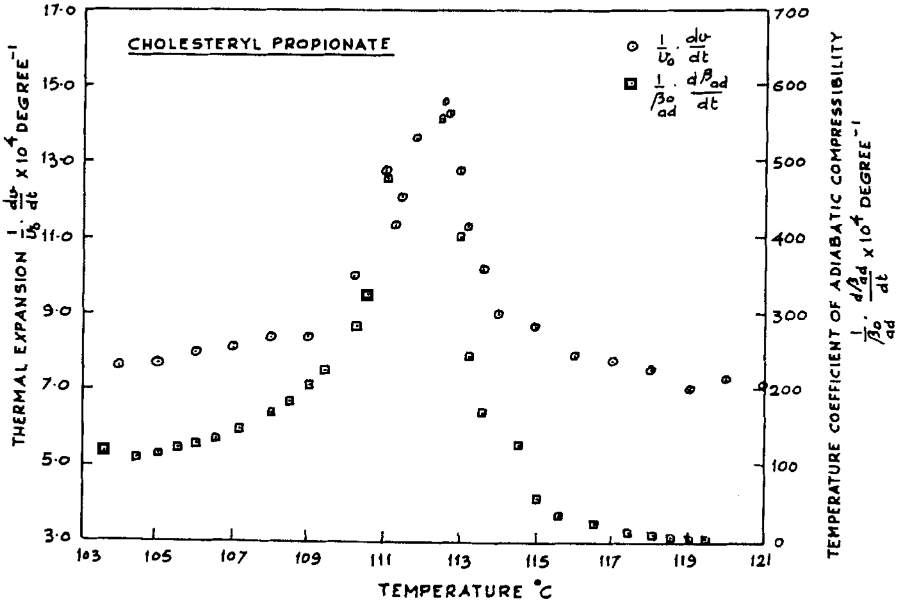


FIGURE 5 Temperature variation of $\frac{1}{v_0}\frac{dv}{dt}$ and $\frac{1}{\beta_0}\frac{d\beta}{dt}$ in cholesteryl propionate.

the changes in R at cholesteric-smectic and isotropic-cholesteric transitions are 51, 49 and 30 and 55 respectively. It is seen from these values that R is remarkably constant with temperature in all the three liquid crystals, the overall variation being only 0.7% in the case of cholesteryl propionate, 0.8% in the case of laurate and 1.5% in the case of myristate.

A study of thermal expansion α_v with temperature in cholesteryl propionate on either side of the isotropic-cholesteric transition indicates that it increases enormously and attains a high value near transition, while it drops rapidly with temperature on either side of transition and the variation is nearly symmetrical. Though the parameter α_β also attains high values near the transition and drops on either side of transition, it exhibits asymmetrical variation. In the cae of laurate and myristate the variation of α_v and α_β are estimated at both the transition temperatures T_c and T_s. A study of the results in cholesteryl laurate, indicates that the thermal expansion attains high values at both the isotropic-cholesteric and the cholesteric-smectic transitions, and on either side of each transition the variation is asymmetrical.

In cholesteryl myristate, at both the transitions T_c and T_s, α_v attains unusually high values, dropping rapidly on either side of the transition and the variation is asymmetrical; on the other hand the parameter α_β near the

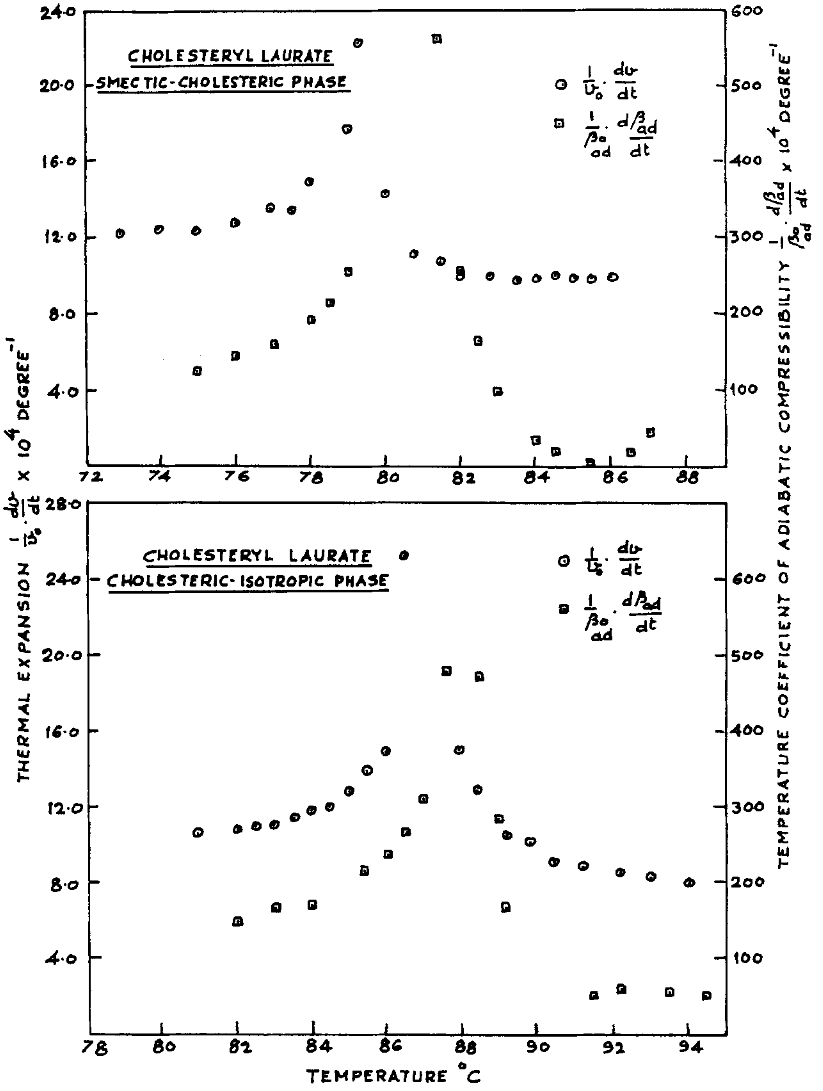


FIGURE 6 Temperature variation of $\frac{1}{v_0}\frac{dv}{dt}$ and $\frac{1}{\beta_0}\frac{d\beta}{dt}$ in cholesteryl laurate.

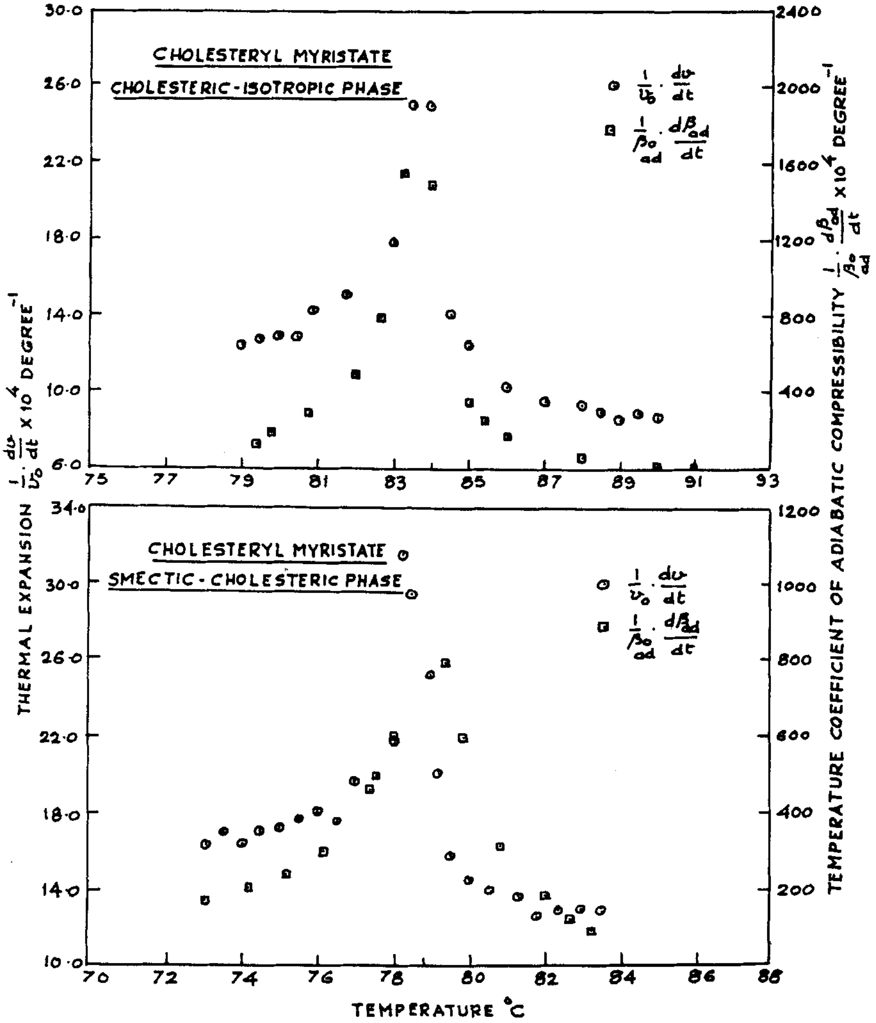


FIGURE 7 Temperature variation of $\frac{1}{v_0}\frac{dv}{dt}$ and $\frac{1}{\beta_0}\frac{d\beta}{dt}$ in cholesteryl myristate.

isotropic-cholesteric transition attains a high value and its variation on either side of the transition is symmetrical while near smectic-cholesteric transition though it attains a high value the variation is asymmetrical on either side of the transition. It is interesting to note that in all these liquid crystals near each transition the ($\alpha_v - t$) and ($\alpha_\beta - t$) curves corresponding to low temperature region lie above the curves corresponding to high temperature region. In computing α_v, v_0 is not taken at the transition temperature but at the temperature corresponding to the mean point of the actual jump, while computing α_β, β_0 is taken at the temperature where the velocity is minimum.

The ultrasonic velocity and adiabatic compressibility have structural effects. The sharp decrease in ultrasonic velocity, and an associated abrupt jump in adiabatic compressibility at the cholesteric-smectic and isotropic-cholesteric transitions must be due to the change in the degree of order of the molecular assembly. According to the theory of Maier and Saupe[12] the degree of molecular orientation is denoted by a parameter S given by:

$$S = \left(\frac{3\,\overline{\mathrm{Cos}^2\,\theta} - 1}{2}\right)$$

where θ is the angle between the long axis of a molecule and the axis of preferred orientation. For the isotropic liquids $S = 0$ and for cholesteric liquid crystals, it lies between 0.3 and 0.8 and for smectic phase, between 0.8 and 0.95. A study of the ultrasonic velocity behaviour in cholesteryl laurate and myristate suggests that these two liquid crystals must have been characterised by low values of S in their cholesteric phase, when compared to cholesteryl stearate, because the velocity dips produced at their isotropic-cholesteric transitions are much less than that of the latter. Further, the fact that the myristate and laurate exhibits prominent dips at their cholesteric-smectic transitions indicates that there must have been large change in the degree of order of the molecular assembly and correspondingly a considerable change in the value of S; in these two liquid crystals the smectic phase appears to have a high value of S compared to that of cholesteryl stearate.

The unusual high values of α_v and α_β near phase transition indicate the presence of large magnitude of pretransitional effects. The behaviour of these compounds at phase transitions is similar to that of liquid-vapour systems near their critical temperature and critical solution near their critical solution temperature. Hence it is proposed to investigate ultrasonic absorption and isothermal compressibility near phase transition and the results will be interpreted in the light of Fixman's theory and other recent theories of phase transitions.

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