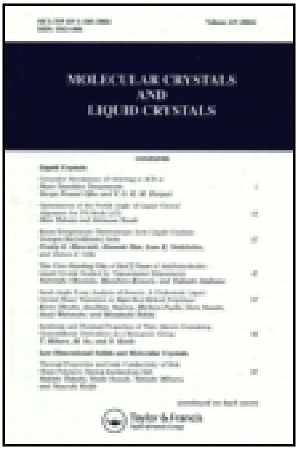

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Ultrasonic Studies in Cholesteryl Myristate-Cholesteryl Propionate Liquid Crystalline Mixtures

A. K. George [a] & A. R. K. L. Padmini [a]

[a] Applied Physics Department, Faculty of Technology and Engineering, M. S. University of Baroda, Baroda, 390 001, India.

Version of record first published: 20 Apr 2011.

To cite this article: A. K. George & A. R. K. L. Padmini (1981): Ultrasonic Studies in Cholesteryl Myristate-Cholesteryl Propionate Liquid Crystalline Mixtures, Molecular Crystals and Liquid Crystals, 65:3-4, 217-226

To link to this article: http://dx.doi.org/10.1080/00268948108082135

Mol. Cryst. Liq. Cryst., 1981, Vol. 65, pp. 217-226
0026-8941/81/6504-0217$06.50/0

Ultrasonic Studies in Cholesteryl Myristate-Cholesteryl Propionate Liquid Crystalline Mixtures

A. K. GEORGE and A. R. K. L. PADMINI

Applied Physics Department, Faculty of Technology and Engineering, M.S. University of Baroda, Baroda—390 001, India.

(*Received April 21, 1980*)

Mixtures of Cholesteryl Myristate (CM) and Cholesteryl Propionate (CP) were studied at four different concentrations. CM exhibits smectic, cholesteric and blue phases, while CP is a cholesteric liquid crystal. Addition of CP to CM disrupts the smectic phase while it enhances the cholesteric and blue phases. Ultrasonic velocity (V) was measured in all the mixtures besides the pure ones using fixed path double crystal interferometer at a frequency of 2 MHz. Specific volume (v) was measured using a special dilatometer designed for the study of liquid crystals. The parameters, viz., adiabatic compressibility (K_{ad}) and molar sound velocity (R) were also estimated. Anomalous behaviour was observed in all the parameters, viz., V, v, K_{ad} and R. The results are interpreted on the basis of McMillan's and Lee's theories. The mean interaction parameter $\bar{\alpha}$ was estimated for different mixtures and found to decrease with increasing concentration of CP in the mixture. It was observed that the cholesteric-smectic A transition becomes second order when $\bar{\alpha} = 0.78$ which is in agreement with McMillan's predictions.

INTRODUCTION

Investigation of the physical properties of liquid crystalline mixtures at mesophase-mesophase and mesophase-isotropic phase transitions is important as it gives deep insight into the nature of the phase transition. Accordingly, considerable work has been done in studying the liquid crystalline mixtures by investigating the optical properties,[1,2] electrical properties,[3,4] viscous properties[5,6] and ultrasonic velocity and absorption.[7]

Cholesteryl myristate (CM) exhibits blue, cholesteric and smectic A phases.[8] Demus *et al.*[9] have reported density measurements in the smectic, cholesteric and blue phases of CM and have drawn the conclusion that smectic-cholesteric and blue-isotropic transitions are of first order and the cholesteric-blue transition is of second order. We have focused our attention to the study of isotropic-blue, blue-cholesteric and cholesteric-smectic transitions. The object of the present investigation is to study ultrasonic velocity and related parameters in smectic, cholesteric and especially blue phase where hardly any ultrasonic studies have been reported. Cholesteryl propionate (CP) is mixed with CM with a view to disrupt the smectic phase of CM. Incidentally, when CP is mixed with CM, the blue phase region is enhanced.

EXPERIMENTAL

The liquid crystals, viz., CM and CP were procured from M/s Aldrich Chemical Co., U.S.A. and were purified by recrystallization. Ultrasonic velocity was measured at a frequency of 2 MHz using a fixed path double crystal interferometer. Specific volume was measured using a special dilatometer designed for the study of liquid crystals. The details of the set-up used for velocity and specific volume measurements and the method followed in preparing the liquid crystalline mixtures are described elsewhere.[10] The melting and transition temperatures were measured using a polarizing microscope equipped with a Mettler FP-2 heating stage. The temperature was controlled to ±0.05°C using a mercury-nitrobenzene thermostat. The velocity measurements are accurate to 1 m/sec and the specific volume to 0.0001 cc/gm.

RESULTS AND DISCUSSION

Ultrasonic velocity, specific volume and other related parameters were estimated in CM, CP and their mixtures at four different concentrations. These parameters were studied throughout the mesomorphic region and 10°C beyond transition in the isotropic region with special attention to the measurements near the phase transition. The mixtures studied are given in Table I along with their melting points, transition temperatures and mesomorphic range. A study of the results in Table I shows that the mesomorphic ranges of blue and cholesteric phases increased with the addition of CP, while the range of smectic phase decreased considerably and vanished at 22.3 mole percent of CP. The mesomorphic range of blue phase increased from 0.3 to 5°C, while that of cholesteric phase increased from 4.9 to 25°C. Obviously, the large increase in the mesomorphic range of the latter phase is due to the change of smectic phase to the cholesteric phase, in addition to

TABLE I

Melting point, transition temperatures and mesomorphic ranges of CM, CP and their mixtures

Mix. no.	Concentration in mole percent	Melting and transition temperatures (in °C)				Mesomorphic range (in °C)		
		T_M	T_B	T_C	T_S	Blue	Cholesteric	Smectic
	100 CM	72.9	84.3	84.0	79.0	0.3	5.9	6.0
Mix. 1	86.97CM + 13.03CP	67.5	80.3	80.0	70.0	0.3	10.0	2.5
Mix. 2	74.80CM + 25.20CP	63.0	84.0	80.0	—	4.0	17.0	—
Mix. 3	63.37CM + 36.63CP	58.5	84.0	79.0	—	5.0	21.5	—
Mix. 4	42.64CM + 57.36CP	56.0	86.0	81.0	—	5.0	25.0	—
	100 CP	102.0	—	112.0	—	—	10.0	—

T_M—Melting point. T_B—Isotropic-blue transition temperature. T_C—Blue-cholesteric or isotropic-cholesteric transition temperature. T_S—Cholesteric-smectic transition temperature.

the already existing cholesteric phase, thus covering the entire region between melting point and blue-cholesteric transition temperature.

The results of ultrasonic velocity, specific volume and adiabatic compressibility for CM, CP and their mixtures are presented in Figures 1 to 6. Figure 1 shows the trend of variation of ultrasonic velocity, specific volume and adiabatic compressibility for CM. The velocities have shown abrupt dips and specific volumes sudden jumps at the major transitions, viz., isotropic-cholesteric and cholesteric-smectic. As the blue phase occurs only for 0.3°C, neither the velocity dip, nor the specific volume jump could be observed at the isotropic-blue transition because the temperature control used has an accuracy of only ± 0.05°C. Adiabatic compressibility is linear both in the isotropic and anisotropic regions away from transition, but exhibited abrupt jumps at both the transitions.

In the case of CP (Figure 2), the ultrasonic velocity is found to show an abrupt minimum of 25 m/sec at isotropic-cholesteric transition. The specific volume shows a remarkable linear variation both in the cholesteric and isotropic phases away from transition, but exhibits a volume jump of 0.0015 cc/gm at the isotropic-cholesteric transition. Adiabatic compressibility shows an abrupt maximum of 2.8×10^{-12} cm^2/dyne at the transition.

Figure 3 shows the variation of ultrasonic velocity, specific volume and adiabatic compressibility for mixture-1. The mixture exhibits blue, cholesteric and smectic phases. Anomalies were observed in all the above parameters at the major phase transitions. No anomally could be observed at the blue-cholesteric transition as it occurs over a narrow range of 0.3°C as in the case of CM.

Figure 4 gives the temperature variation of ultrasonic velocity, specific volume and adiabatic compressibility for mixture-2. The mixture exhibits

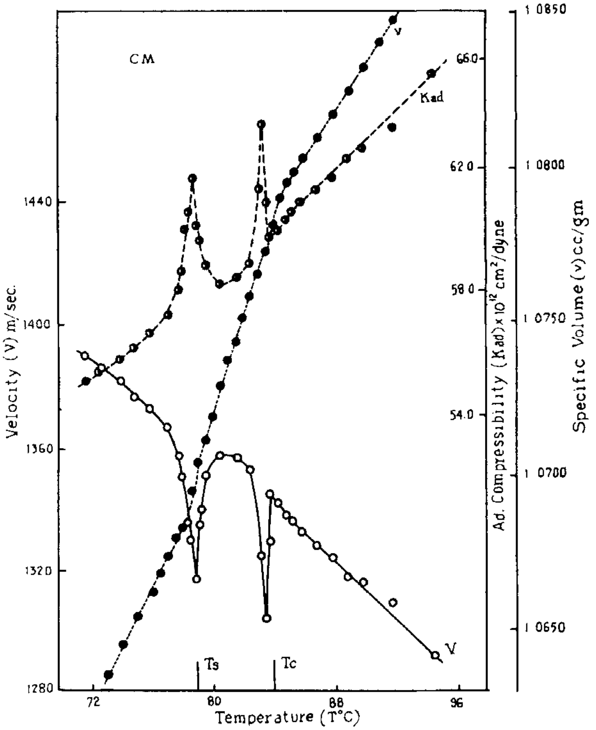

FIGURE 1 Ultrasonic velocity (V), specific volume (v) and adiabatic compressibility (K_{ad}) against temperature (T) for CM.

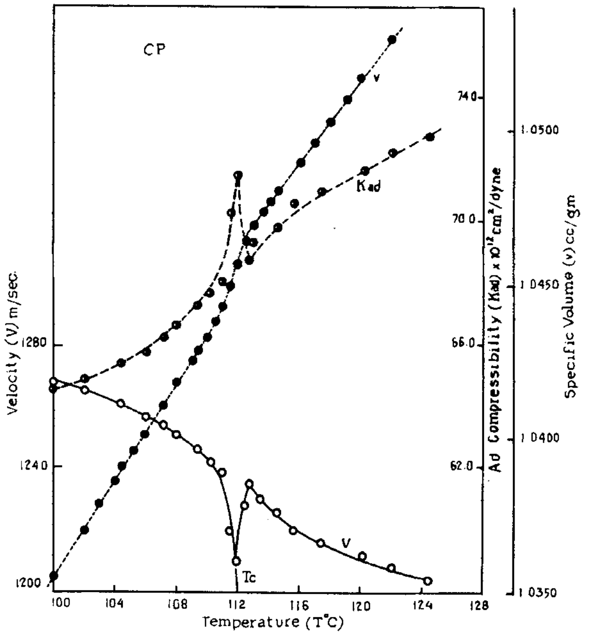

FIGURE 2 Ultrasonic velocity (V), specific volume (v) and adiabatic compressibility (K_{ad}) against temperature (T) for CP.

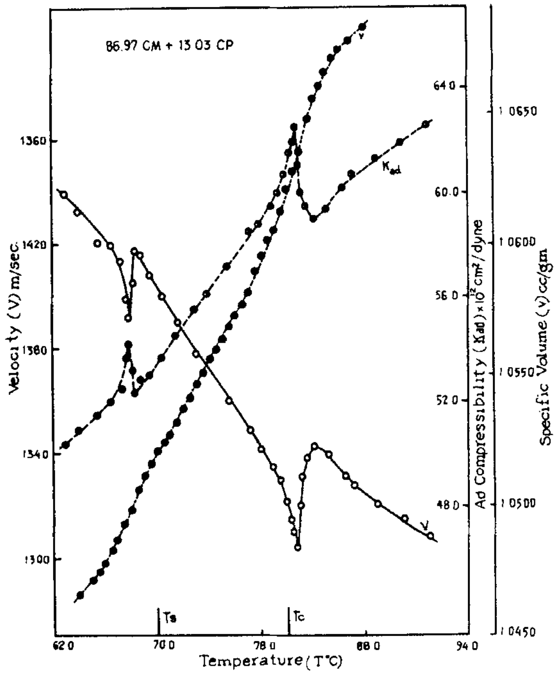

FIGURE 3 Variation of the same parameters as in Figure 1 for Mix. 1.

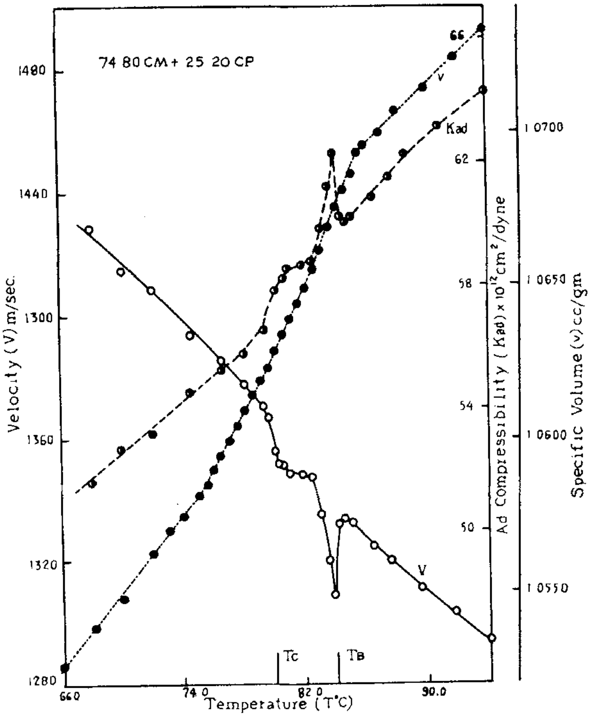

FIGURE 4 Variation of the same parameters as in Figure 1 for Mix. 2.

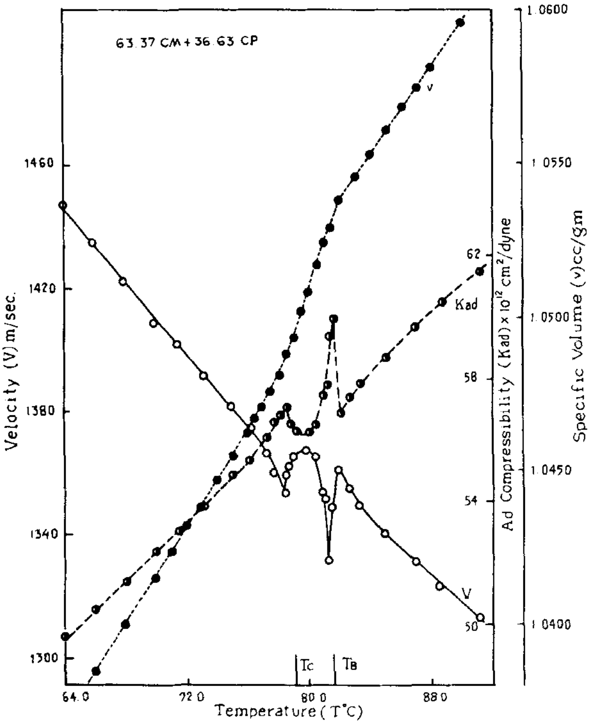

FIGURE 5 Variation of the same parameters as in Figure 1 for Mix. 3.

cholesteric and blue phases. Ultrasonic velocity has shown a dip of 16 m/sec at isotropic-blue transition, while at the blue-cholesteric transition, the velocity remained stationary over a range of 2°C and then increased sharply. The specific volume has shown a jump of 0.0007 cc/gm at the isotropic-blue transition and a change of slope at the blue-cholesteric transition. Adiabatic compressibility has shown a jump of 2.3 × 10^{-12} cm^2/dyne at the isotropic-blue transition. No remarkable change at the blue-cholesteric transition was observed and it remained constant over a range of 2°C in the vicinity of the transition.

Figures 5 and 6 show the temperature variation of ultrasonic velocity, specific volume and adiabatic compressibility for mixtures 3 and 4. For mixture-3, ultrasonic velocity has shown a dip of 30 m/sec and 14 m/sec at isotropic-blue and blue-cholesteric transitions, respectively. Specific volume exhibits a jump of 0.0008 cc/gm at the isotropic-blue transition and a change of slope at the blue-cholesteric transition. Adiabatic compressibility has shown jumps of 2.5 × 10^{-12} cm^2/dyne and 0.8 × 10^{-12} cm^2/dyne at the isotropic-blue and blue-cholesteric transitions, respectively. For mixture-

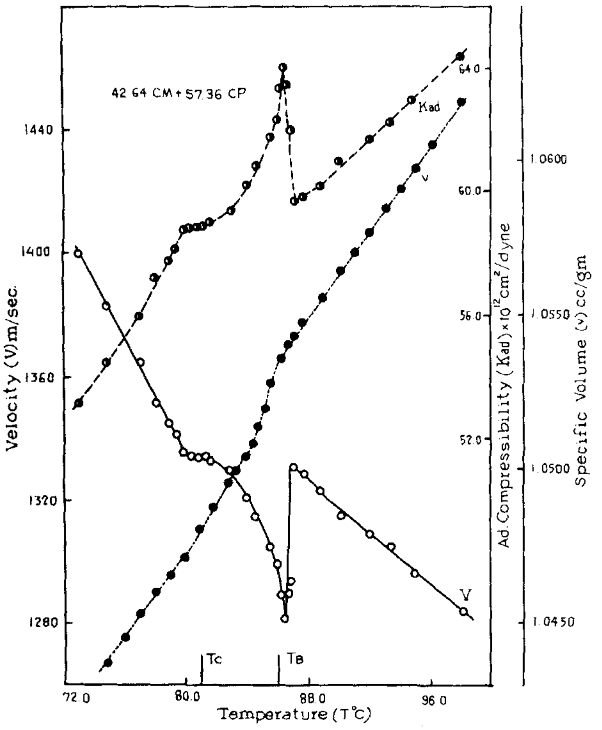

FIGURE 6 Variation of the same parameters as in Figure 1 for Mix. 4.

4, ultrasonic velocity has shown a dip of 49 m/sec at the isotropic blue transition, but remained constant over a range of 1.5°C in the blue-cholesteric transition region. Specific volume showed a jump of 0.0008 cc/gm at the isotropic-blue transition and a change of slope at blue-cholestric transition. Adiabatic compressibility has shown a jump of 4.5×10^{-12} cm^2/dyne at isotropic-blue transition. No considerable change was observed at the blue-cholesteric transition.

Figures 7 and 8 give the variation of molar sound velocity with temperature for CM, CP and their mixtures. A glance at the figures reveal that molar sound velocity remains constant away from the phase transition and show anomalies at the phase transitions.

We have examined the results on specific volume of CM and CM + CP mixture on the light of McMillan's[11] and Lee's[12] theories following Muller and Stegemeyer.[13] The change in specific volume Δv at the cholesteric-smectic A transition is estimated in CM and those mixtures in which smectic phase is present by extrapolating the linear portion of v against T curve in the smectic phase to the transition temperature T_s and measuring v_s cor-

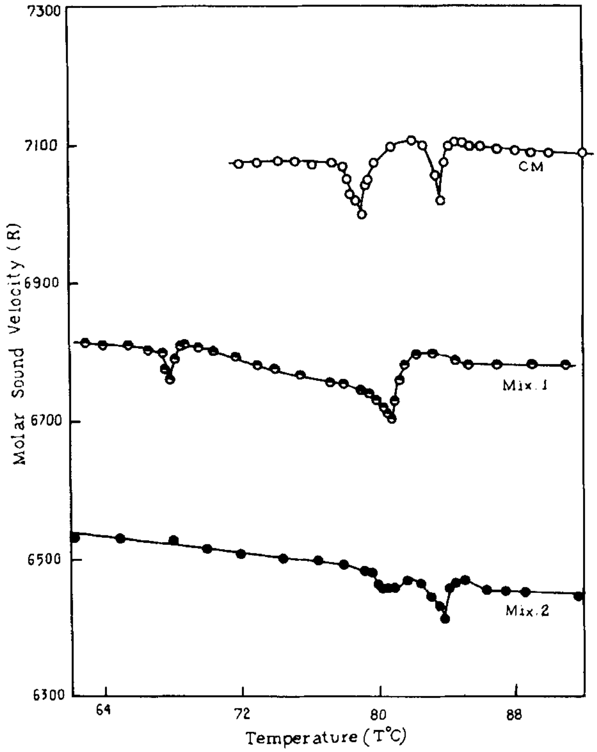

FIGURE 7 Molar sound velocity (R) against temperature (T) for CM, Mix. 1 and Mix. 2.

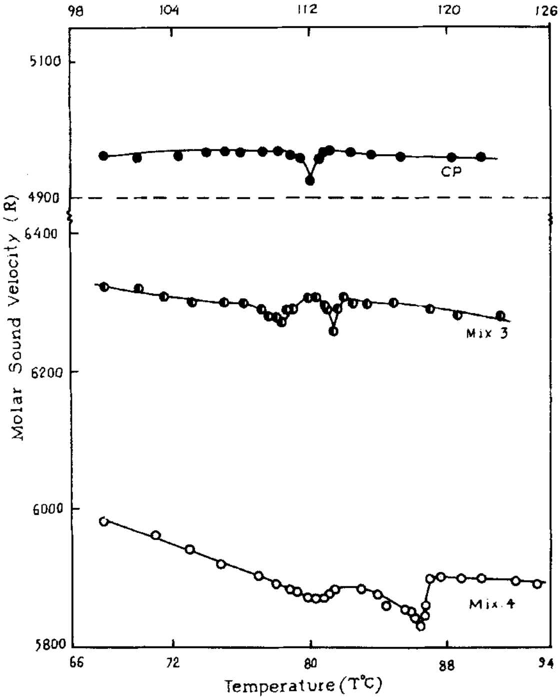

FIGURE 8 Molar sound velocity (R) against temperature (T) for CP,, Mix. 3 and Mix. 4.

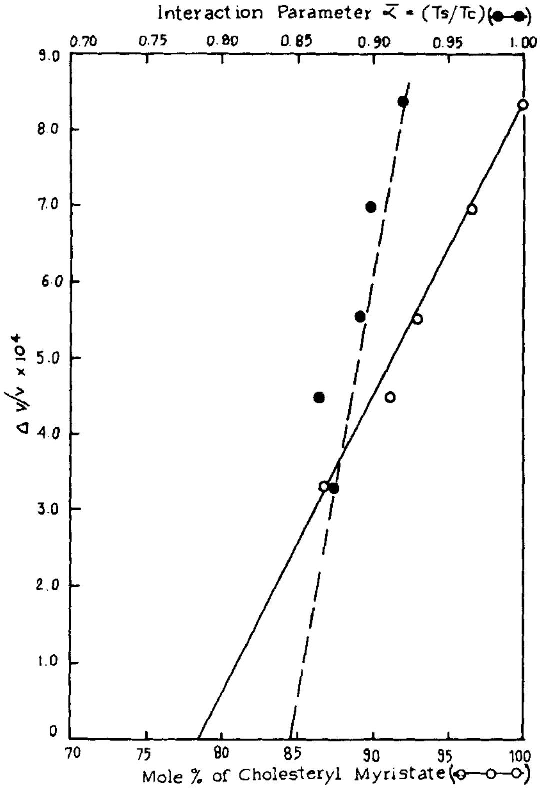

FIGURE 9 $\Delta v/v$ against mole percent of CM and interaction parameter $\bar{\alpha}$ against $\Delta v/v$.

responding to T_s and v_c is measured at the transition temperature T_s directly. The mean value of v_c and v_s are taken as v and the difference as Δv and the ratio of $\Delta v/v$ is plotted versus mole percent of CM in the mixture. To get more points in the plot, specific volume is measured at four more concentrations other than mentioned in Table I in which smectic phase exists and the values of v_c and v_s are estimated as mentioned above. It is seen from Figure 9 that the plot is remarkably linear and when extrapolated, $\Delta v/v$ becomes zero at 78.5 mole percent of CM. Possibly, at this concentration of the mixture, the second order transition might have occurred.

According to McMillan.[11] the nature of cholesteric-smectic A transition is expected to depend merely on the interaction parameter $\bar{\alpha}$ given by

$$\bar{\alpha} = 2\exp\left[-\left(\frac{\pi r_0}{a}\right)^2\right]$$

describing the anisotropic interaction of the rigid central section of the molecule (r_0) resulting in a layer arrangement of distance "a." The flexible end groups of the molecules represented by alkyl chain in the case of CM only determine the interplanar distance. As McMillan[11] states that this function could be performed also by other molecules, it can be assumed that the interaction parameter in the mixture can be described by a mean interaction parameter $\bar{\alpha}(x)$ depending on the mole fraction which can be estimated from the ratio of transition temperatures, T_{CS}/T_{CI}. The value of $\bar{\alpha}$ was estimated for different mixtures and found to decrease with increasing concentration of CP. When $\bar{\alpha}$ was plotted against $\Delta v/v$ (Figure 9) for CM and different mixtures it was found to be remarkably linear. When it was extrapolated, for $\Delta v/v = 0$, $\bar{\alpha}$ is equal to 0.78. McMillan[11] has predicted that cholesteric-smectic A transition becomes second order when $\bar{\alpha} \leq 0.88$. The value (0.78) obtained here is in agreement with McMillan's theory.[11] From the above results, it is interesting to conclude that addition of CP to CM have affected cholesteric-smectic A transition and changed it from first order to second order at a particular concentration.

Acknowledgment

The authors are thankful to Prof. R. V. Joshi and Dr. R. A. Vora for their interest in this work. Financial Assistance of the University Grants Commission is acknowledged.

References

1. J. Adams, W. Haas, and J. Wysocki, *Mol. Cryst. Liq. Cryst.*, **8**, 9 (1969); *Phys. Rev. Lett.*, **22**, 92 (1969).
2. P. Adamski and A. Dylik-Gromiec, *Mol. Cryst. Liq. Cryst.*, **25**, 281 (1974).
3. G. H. Heilmeier and J. E. Goldmacher, *Applied Phys. Lett.*, **13**, 132 (1968); *Proc. I.E.E.E.*, **57**, 34 (1969).
4. W. Haas, J. Adams, and G. Dir., *Chem. Phys. Lett.*, **14**, 95 (1972).
5. R. S. Porter and C. Griffin, *Mol. Cryst. Liq. Cryst.*, **25**, 131 (1974).
6. E. Fukada, *Symp. Rheology of Liq. Cryst. Saitama, Japan*, (1975).
7. G. G. Natale, *Ultrasonic Symp. Proc.*, **366** (1977); *J. Acoust. Soc. America*, **63**, 1677 (1978) (Review article).
8. D. Coates and G. W. Gray, *Phys. Lett.*, **45A**, 115 (1973).
9. D. Demas, H.-G. Hahn, and F. Kuschel, *Mol. Cryst. Liq. Cryst.*, **44**, 61 (1978).
10. C. G. Kartha and A. R. K. L. Padmini, *Mol. Cryst. Liq. Cryst.*, **29**, 243 (1975).
11. W. L. McMillan, *Phys. Rev.*, **A4**, 1238 (1971); *Phys. Rev.*, **A6**, 936 (1972); *Phys. Rev.*, **A7**, 1419 (1973).
12. F. T. Lee, H. T. Tan, Y. M. Shin, and C. N. Woo, *Phys. Rev. Lett.*, **31**, 1117 (1973).
13. W. U. Muller and H. Stegemeyer, *Chem. Phys. Lett.*, **27**, 130 (1974).