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Divergence of Cholesteric Pitch Near the Smectic-A Transition in Some Cholesteryl Nonanoate Binary Mixtures

Shu-Hsia Chen [a c d] & J. J. Wu [b]

[a] Department of Electrophysics

[b] Institute of Electro-Optical Engineering, National Chiao-Tung University, Hsinchu, Taiwan, 300, Republic of China

[c] Physical Society of the Republic of China at National Chiao-Tung University, February 15-6 1981

[d] Lawrence Berkeley Laboratory, University of California, Berkeley, California, 94720

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Divergence of Cholesteric Pitch Near the Smectic-A Transition in Some Cholesteryl Nonanoate Binary Mixtures†‡

SHU-HSIA CHEN‡§
Department of Electrophysics

and

J. J. WU
Institute of Electro-Optical Engineering, National Chiao-Tung University, Hsinchu, Taiwan 300, Republic of China

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The cholesteryl nonanoate-propionate and nonanoate-butyrate binary mixtures were studied at different component ratio. The detailed temperature dependence of the pitch of the cholesteric mesophase was measured. The intrinsic pitch was calculated. The divergence of the pitch near the smectic-A transition shows a power-law behavior. For the cholesteryl nonanoate-propionate mixtures with weight ratios (90:10), (85:15), (80:20) and (75:25) the corresponding values of the critical exponent ν of the power-law are 0.683, 0.675, 0.681 and 0.693 respectively. And those for the cholesteryl nonanoate-butyrate mixtures with weight ratios (90:10), (85:15), (80:20), (75:25) and (70:30) the corresponding values of ν are 0.678, 0.679, 0.668, 0.672 and 0.662. These values agree with de Gennes' prediction.

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§ Present address: Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720.

INTRODUCTION

The pretransitional effect near the nematic or cholesteric to smectic-A transitions in liquid crystals has been studied both theoretically[1-9] and experimentally[10-13] by many authors. The anomalous increase of the elastic constants and cholesteric pitch[14] is believed to be proportional to the coherence length ξ which represents the short-range smectic order in the nematic or cholesteric mesophase. Therefore the cholesteric pitch should have similar temperature dependence of ξ near the effective critical temperature T_c as follows,

$$P = P_n + D(T - T_c)^{-\nu}$$

where P is the apparent pitch, P_n is the intrinsic pitch or the pitch in the absence of the smectic ordering and ν is the critical exponent which is typically between 0.6 and 0.7 from model calculations and experiments. The divergence of the pitch of pure cholesteryl compound were studied by Chen and Chou[15] and other research groups.[16,17]

In this work the cholesteryl nonanoate (CN)-propionate (CP) and cholesteryl nonanoate-butyrate (CBu) binary mixtures were studied. The detailed measurement of the temperature dependence of the cholesteryl mesophase pitch of the mixture at difference component weight ratio are presented. Bak and Labes'[18] equation was used to compute both the molar twisting power for these compounds and the intrinsic pitch of the mixtures. The relation between the molar twisting power and the temperature in the range of cholesteric mesophase of the mixture is discussed. The divergence of pitch at lower temperature of the mixture is explained by the power law and the values of critical exponent is reported.

EXPERIMENTAL METHODS

Cholesteryl nonanoate (CN), cholesteryl propionate (CP) and cholesteryl butyrate (CBu) were purchased from Merck and used in this experiment without further purification. Their transition temperatures were determined by Reichert Thermovar. Cholesteryl propionate (CP) shows a melting point at $T = 96°C$ and a clear point at $T = 114°C$. Cholesteryl butyrate melts to cholesteric mesophase at $T = 99.5°C$ and shows a clearing point at $T = 111°C$. Cholesteryl nonanoate (CN) melts at $T = 80°C$ to cholesteric mesophase and becomes normal liquid at $T = 91°C$. On cooling from the isotropic liquid, CN forms a cholesteric phase at $T = 91°C$ and a smectic-A phase at $T = 74°C$. The mixture was obtained by mixing the cholesteric compounds in chloroform solution. The sample film was made by sandwiching the isotropic mixture between slide glass and cover glass. The glasses were cleaned by cleaning solution and rubbed before used.

The selective reflection technique was used to determine the pitch of the sample. A Schimadzu double beam spectrophotometer was employed to measure the reflected peak of the sample. The sample film was heated by a block heater and arranged perpendicular to the incident light beam. The sample temperature was controlled within 0.1°C and measured with a copper-constantan thermocouple and a HP digital-multimeter. After heated to isotropic liquid the sample was allowed to cool into the cholesteric range and touched to make sure that the planar texture was formed before the data were taken. The reflected wavelength was measured with an accuracy of ±5 Å. The pitch was determined by

$$P = \frac{\lambda}{\bar{n}}$$

where λ is the wavelength of the reflected peak and $\bar{n}$ is the average index of refraction of cholesteric mixture. It seems to be reasonable to use the value of $\bar{n} = 1.5$, since the influence on the pitch due to the temperature dependence of refraction index is quite small when compared with the twisting angle change caused by temperature itself.[19-22]

EXPERIMENTAL RESULTS

The values of the apparent pitch for eight binary mixtures of different weight fraction of *CN* and *CP* are shown in Figure 1, as functions of temperature. Upon cooling, the mixtures with higher concentration of *CN* namely A, B, C and D show extremely high temperature coefficient near the cholesteric-smectic phase transition. And the mixtures with lower concentration of *CN* namely E, F, G, H, I and J remain in cholesteric mesophase up to low temperature before crystalizing. The temperature and composition dependence of pitch for these mixtures in the temperature range far away from the transitions should be related to the molar twisting power of *CN* and *CP* following the equation introduced by Bak and Labes.

The results of another set of binary mixtures namely *CN* and *CBu* are shown in Figure 6. The temperature dependence of the pitch of

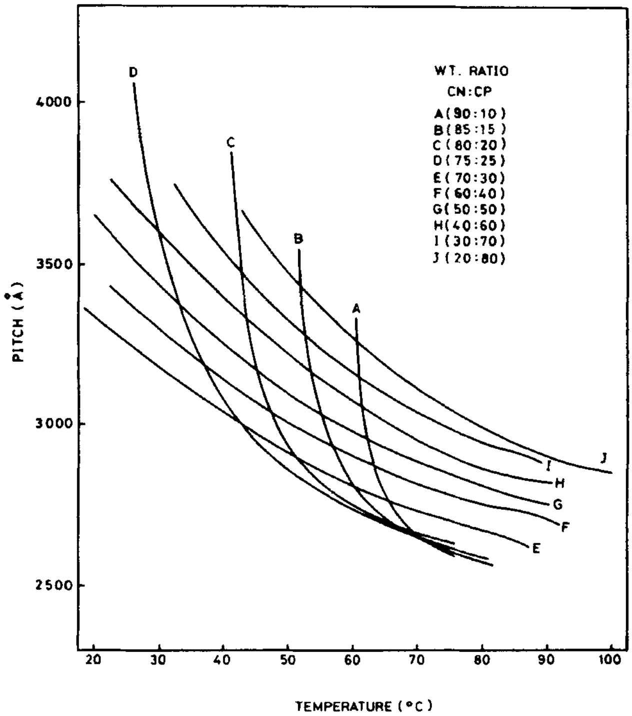

FIGURE 1 Temperature dependence of pitch in cholesteryl nonanoate-propionate mixture at different weight ratio.

these mixtures behave similarly to that of the first set. Upon cooling, the mixtures namely A, B, C, D and E transit from cholesteric mesophase to smectic mesophase and show pretransitional anomalies. Those with lower concentration of *CN* remain in cholesteric mesophase and behave normally up to a low temperature of 40°C.

ANALYSIS OF EXPERIMENTAL DATA

The data of curves E, F, G, H, I and J in Figure 1 which are corresponding to the weight ratio $W_{CP} = 0.3$, 0.4, 0.5, 0.6, 0.7 and 0.8 respectively, were used to compute the molar twisting power by employing the pitch-concentration equation which was derived by Bak and Labes. The equation for binary mixture can be written as:

$$\frac{M_{CP} + (M_{CN} - M_{CP})W_{CP}}{2pd} - N\Delta\beta_{CN,CP}(1 - W_{CP})W_{CP}$$
$$= W\beta_{CN}\frac{M_{CP}}{M_{CN}} + N\left(\frac{M_{CN}}{M_{CP}}\beta_{CP} - \frac{M_{CP}}{M_{CN}}\beta_{CN}\right)W_{CP} \quad (1)$$

where W_{CP} = weight fraction of the cholesteryl propionate and N is Avogadros' number

$$d = \frac{d_{CN}}{1 + (d_{CN}/d_{CP} - 1)W_{CP}}$$

is the density (g/cm^3) of the mixture and $d_{CP(CN)}$ is the density of the cholesteryl propionate (nonanoate). The parameter $\Delta\beta_{CP,CN}$ is defined as:

$$\Delta\beta_{CP,CN} = 2\beta_{CP,CN} - \left[\left(\frac{M_{CN}}{M_{CP}}\right)\beta_{CP} + \left(\frac{M_{CP}}{M_{CN}}\right)\beta_{CN}\right]$$

where $\beta_{CP(CN)}$ is the effective (or mean) molecular twisting power between $CP(CN)$ molecules only. When β is positive (negative), the helical structure is right (left) handed. In Eq. (1) the left hand side is linear with respect to W_{CP} and the plot is shown in Figure 2. The values $d = 1$ g/cm^3, $M_{CP} = 443$ g and $M_{CN} = 527$ g were used. The value of $N\Delta\beta_{CN,CP}$ was adjusted using the least square method so that the data fall on a straight line. By extrapolating the straight lines in Figure 2 to $W_{CP} = 0$ and 1, the molar twisting powers $N\beta_{CN,CN}$ and $N\beta_{CP,CP}$ for different temperatures are obtained. Figure 3 and 4 show the variation of molar twisting power with temperature obtained in this manner.

The twisting power obtained in this way was put into Eq. (1) to calculate the intrinsic pitch P_n for each of the binary mixtures of weight ratio $W_{CP} = 0.10$, 0.15, 0.20 and 0.25. The divergence of the pitch of the mixture near it's transition point to smectic phase was obtained as the difference of the apparent pitch, the values of curves A, B, C and D in Figure 1, and the corresponding intrinsic pitch. The data show a power-law behavior according to the equation proposed by de Gennes as follows,

$$P = P_n + D(T - T_c)^{-\nu}$$

where ν = critical exponent describing the divergence of the smectic

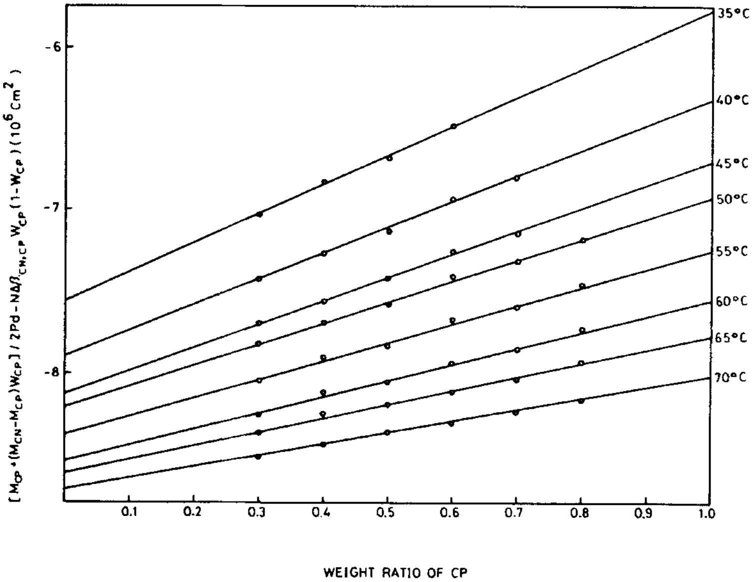

FIGURE 2 Plot of $M_{CP} + (M_{CN} - M_{CP})W_{CP}/2pd - N\Delta\beta_{CP,CN}W_{CP}(1 - W_{CP})$ vs weight ratio (W_{CP}) of cholesteryl propionate at different temperatures.

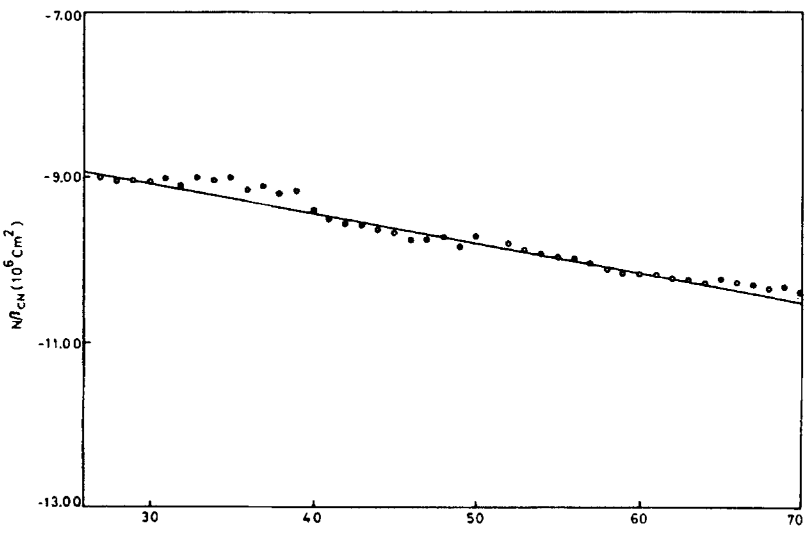

FIGURE 3 Temperature dependence of molar twisting power of cholesteryl nonanoate obtained from the study of *CN-CP* mixture.

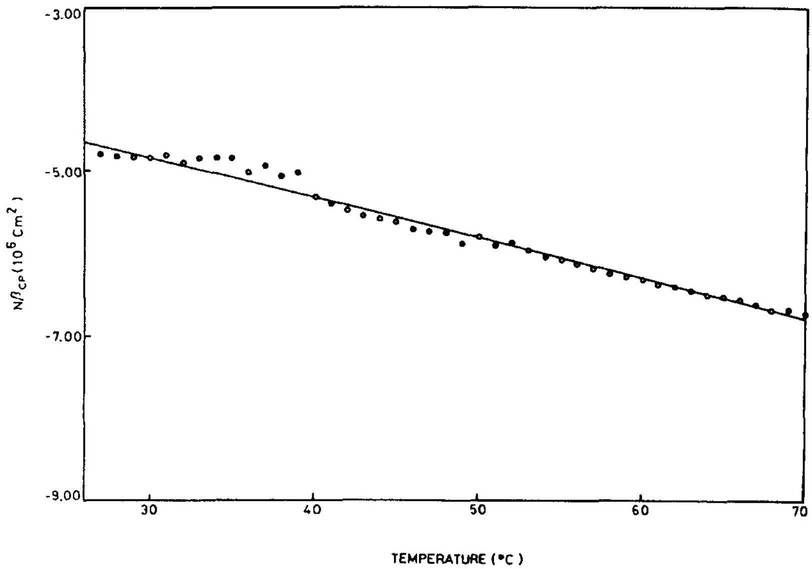

FIGURE 4 Temperature dependence of molar twisting power of cholesteryl propionate.

correlation lengths; P = the apparent pitch of the mixture; P_n = the intrinsic pitch of the mixture and T_c = the effective critical temperature. The plot of log $(P - P_n)$ vs log $(T - T_c)$ is shown in Figure 5. They are straight lines and their slopes give the values of $-\nu$. The results and corresponding T_c are shown in Table I.

The analysis of the second set (*CN* and *CBu* mixture) data which is shown in Figure 6 is essentially the same as stated above. The data of curves F, G, H, I, J, K and L in Figure 1 which are corresponding to the weight ratio W_{CBu} = 0.40, 0.45, 0.50, 0.55, 0.60, 0.65 and 0.70 respectively, were used to compute the molar twisting power by employing the equation of Bak and Labes. The values M_{CBu} = 457 g were used. The linear relation is shown in Figure 7. The obtained molar twisting powers, $N\beta_{CN,CN}$ and $N\beta_{CBu,CBu}$ are shown in Figure 8 and 9. The intrinsic pitch P_n for each of the binary mixtures of weight ratio W_{CBu} = 0.10, 0.15, 0.20, 0.25 and 0.30 were calculated.

The values of curves A, B, C, D and E in Figure 6 were employed to show the divergence of the pitch. The plot of log $(P - P_n)$ vs log $(T - T_c)$ is shown in Figure 10. The effective critical temperature T_c and the value of critical exponent ν corresponding to each weight ratio W_{CBu} are shown in Table II.

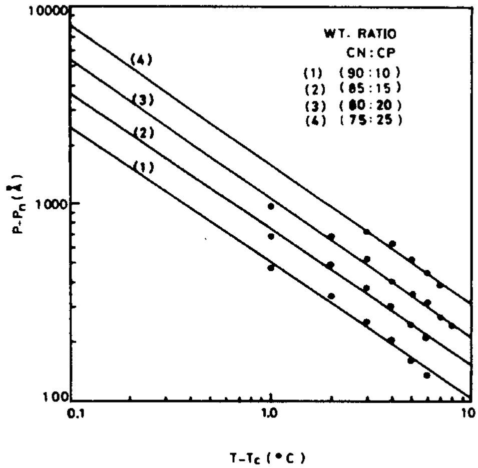

FIGURE 5 Plot of log $(P - P_n)$ vs $(T - T_c)$ for cholesteryl nonanoate-propionate mixtures.

DISCUSSION

After the value of $N\Delta\beta_{CN,CP(CBu)}$ being adjusted, the pitch of the mixture with high concentration of $CP(CBu)$ shown in Figure 1 (Figure 6) has a linear relation to the weight ratio of $CP(CBu)$ for a wide temperature range as in Figure 2 (Figure 7). Therefore the molar twisting powers $N\beta_{CN}$ and $N\beta_{CP(CBu)}$ can be found by extrapolating the straight line to $W_{CP(CBu)} = 0$ and 1 for the same temperature range. It is clear as shown in Figure 3 (8) and 4 (9) that the temperature dependence of the molar twisting power is linear. This result is consistent with what Chen and Chou[23] reported before. In other

TABLE I

The effective critical temperature and value of critical exponent of cholesteryl nonanoate and propionate mixture at different weight ratio.

Weight ratio of CP W_{CP}	Effective critical temperature T_c	Critical exponent ν
0.10	60°C	0.683
0.15	51°C	0.675
0.20	41°C	0.681
0.25	24°C	0.693

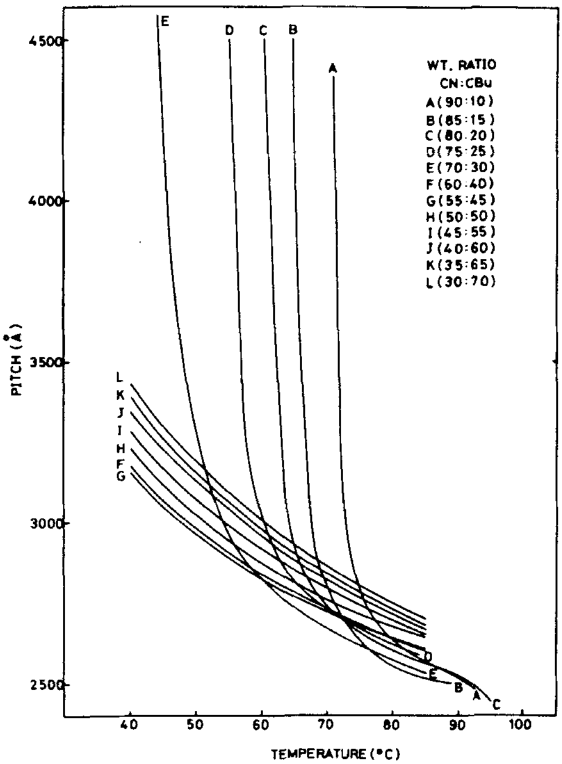

FIGURE 6 Temperature dependence of pitch in cholesteryl nonanoate-butyrate mixture at different weight ratio.

words, the intrinsic pitch is inversely proportional to the temperature as predicted by Keating[24] in a temperature range far away from the transition.

The intrinsic pitch for mixture of low *CP*(*CBu*) weight ratio (i.e. high *CN* concentration), which was calculated by using Eq. (1) with the adjusted value of $N\beta_{CN,CP(CBu)}$ and the molar twisting power estimated from Figure 2, (Figure 7) was far away from the apparent pitch near the smectic transition. This anomalous result is due to the pretransitional effect. The divergence of the pitch can be represented by the critical exponent ν. The values of ν for four weight ratios of *CP* are 0.683, 0.675, 0.681 and 0.693 and for five weight ratios of *CBu* are 0.678, 0.679, 0.668, 0.672 and 0.662 which are very close to the value for pure *CN* obtained by Chen and Chou. It is also in agreement with the values obtained by elastic constant measurement and de Gennes'

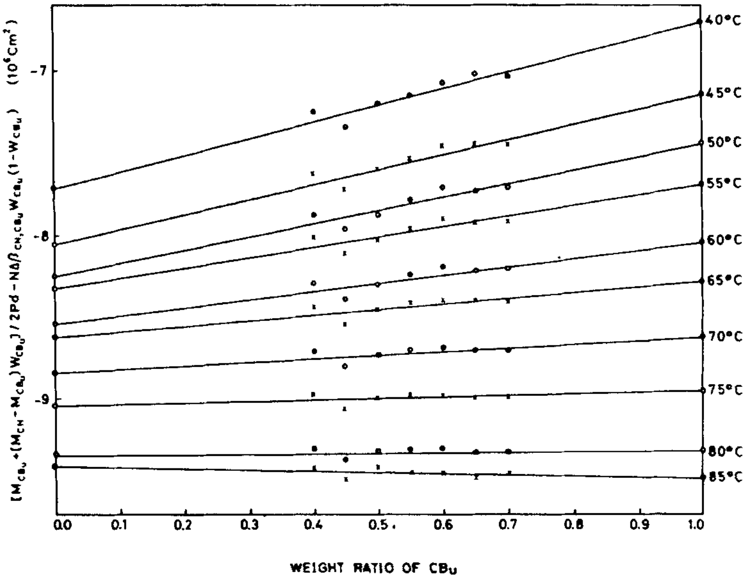

FIGURE 7 Plot of $M_{CBu} + (M_{CN} - M_{CBu})W_{CBu}/2pd - N_{CBu,CN}W_{CBu}(1 - W_{CBu})$ vs weight ratio (W_{CBu}) of cholesteryl butyrate at different temperature.

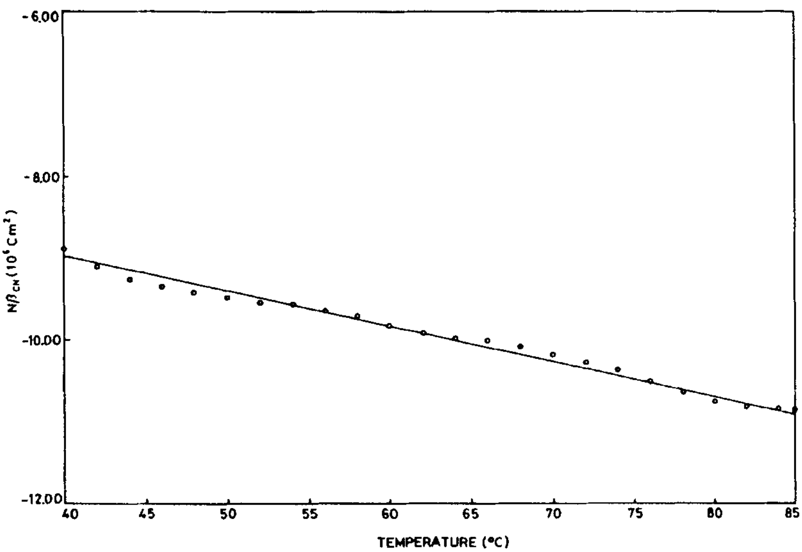

FIGURE 8 Temperature dependence of molar twisting power of cholesteryl nonanoate obtained from the study of *CN-CBu* mixture.

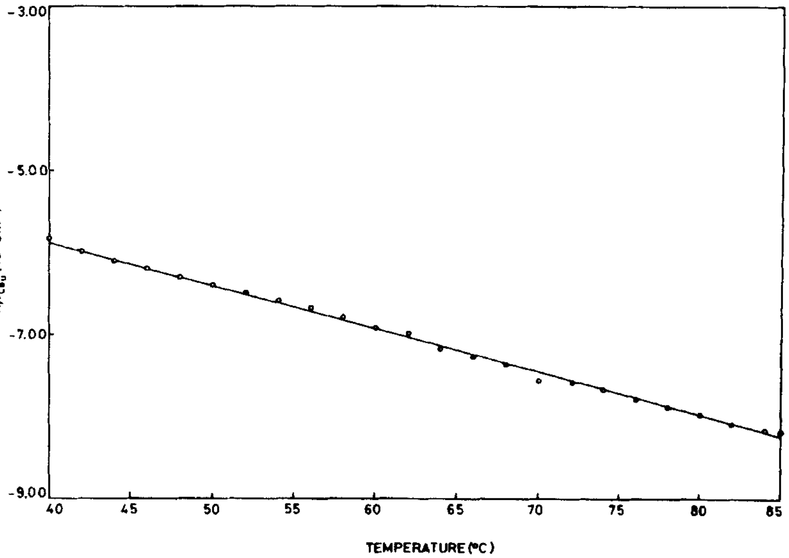

FIGURE 9 Temperature dependence of molar twisting power of cholesteryl butyrate.

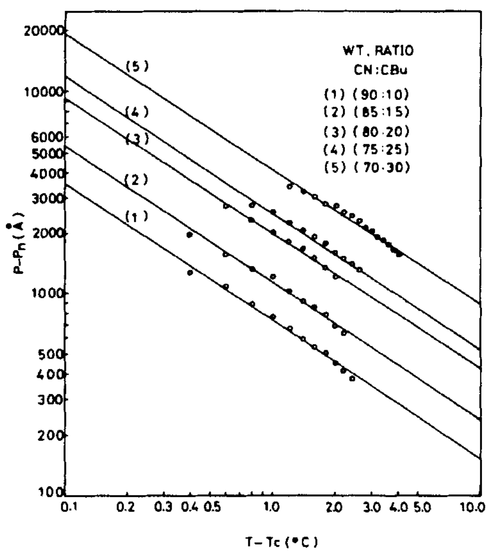

FIGURE 10 Plot of log $(P - P_n)$ vs $(T - T_c)$ for cholesteryl nonanoate-butyrate mixtures.

TABLE II

The effective critical temperature and value of critical exponent of cholesteryl nonanoate and butyrate mixture at different weight ratio.

Weight ratio of *CBu* W_{CBu}	Effective critical temperature T_c	Critical exponent ν
0.10	70.8°C	0.678
0.15	64.4°C	0.679
0.20	59.4°C	0.668
0.25	52.0°C	0.672
0.30	40.0°C	0.662

prediction. Pindak *et al.* also reported the similar value of ν for *CN* and *CD*. It is worthy to notice that the value of ν is quite sensitive to the choice of T_c which is hard to determine precisely.

CONCLUSION

The intrinsic pitch of the binary mixture of *CN* and *CP* (*CBu*) and the twisting power $N\beta_{CN}$ and $N\beta_{CP(CBu)}$ were obtained by using the equation derived by Bak and Labe. The molar twisting power is linear in the cholesteric mesophase temperature range of the mixture. The divergence of the pitch due to the pretransitional smectic effect for the mixture of high *CN* concentration was represented by the value of the critical exponent for the smectic correlation length (ν). The values of ν for the mixtures of $W_{CP} = 0.10, 0.15, 0.20$ and 0.25 being 0.683, 0.675, 0.681 and 0.693 respectively and for mixtures of $W_{CBu} = 0.10$, 0.15, 0.20, 0.25 and 0.30 being 0.678, 0.679, 0.668, 0.672 and 0.662 are in good agreement with the value of pure *CN* reported before by the same group. It is also consistent with the values obtained by the elastic constant measurements and de Gennes' prediction.

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