OPTICALLY DETERMINED MESOMORPHIC TRANSITIONS IN CHOLESTERYL STEARATE AT HIGH PRESSURE

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A new optical method to determine phase transitions at high pressure is described in detail. The method is applied to mesomorphic transitions in cholesteryl stearate. The solid-isotropic liquid and cholesteric-isotropic liquid transition temeperatures vary linearly with pressure in the range of 1 to 800 bar. The volume change computed at 1 bar through the Clapeyron equation is 55 $cm^3 mol^{-1}$ for the solid-isotropic liquid transition and 1.2 $cm^3 mol^{-1}$ for the cholesteric-isotropic liquid transition. The ratio of the latter volume change to the former is 0.022, being close to that for many nematic phases.

Introduction

Liquid crystals have been recently investigated at high pressure by using various kinds of methods; volumetry[1~6], NMR[7~9], DTA[10~16], and optical[17~24], dielectric[11~25], and viscosity[5] measurements. The optical measurement is popular and carried out in a variety of ways. Liquid crystals are usually opaque, so that a strong optical source and a sensitive detector are required for a path length of several mm. Although a photomultiplier is very sensitive and useful for many purposes, it is not so convenient for detecting successive mesomorphic transitions where drastic changes

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(*Received September 12, 1979*)

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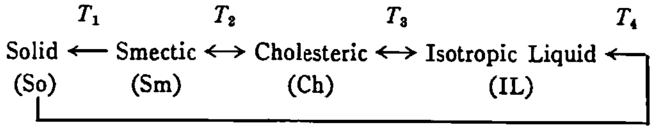
in transparency occur. A phototransistor is useful for the measurement of a wide range of light intensity. In the present work, we used a phototransistor with a He-Ne gas laser, and applied the optical system to mesomorphic transitions in cholesteryl stearate. This compound is known to exhibit the thermotropic mesophases. The transitions are monotropic with respect to the solid as



where $T_1<T_2<T_3<T_4$. The transition temperatures, T_3 and T_4 are determined as a function of pressure up to 800 bar. The obtained results are compared with volumetric ones by Semenchenko *et al.*[2]

Experimental

Cholesteryl stearate was supplied by Tokyo Kasei Co., Ltd. and purified by following the established procedure[26]. The transition temperatures at 1 bar agree well with the reliable values by Davis *et al.* in Table 1, so that the purity of the sample is high enough. When the purity was low, the transition detected by the transparency to the laser was not so sharp.

Table 1. Transition temperatures (°C) in cholesteryl stearate at 1 bar.

	Sell & Neumann[27]	Gray[28]	Ennulat[29]	Barrall *et al.*[30]	Arnold *et al.*[31]	Davis *et al.*[32]	Present work
So-IL	82	83	—	85.0	82	81.8	81.3
Ch-IL	78	79.5	79.2	71.0	77	74.4	75.0
Sm-Ch	74	75.5	75.1	—	72	69.6	—

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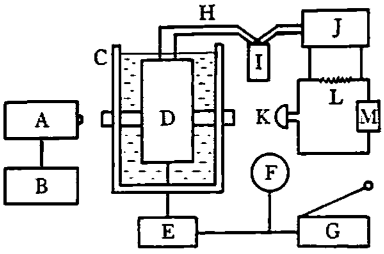

Fig. 1 Schematic diagram of apparatus.
A: Laser tube (NEC GLG2032, 3 mW),
B: Laser power supply,
C: Thermally regulated oil bath,
D: High-pressure optical cell ($\mathrm{H_RC}$,∼45),
E: Pressure reservoir,
F: Bourdon gage (Heise),
G: Hand pump (Hikari Kikai, Ltd.),
H: Thermocouple (chromel-alumel),
I: Ice box,
J: Recorder (Yokogawa 3047, 2 pens),
K: Phototransistor (Toshiba TPS6 03),
L: Resistance (1kΩ),
M: Power supply (National ETU-12P05, 12V).

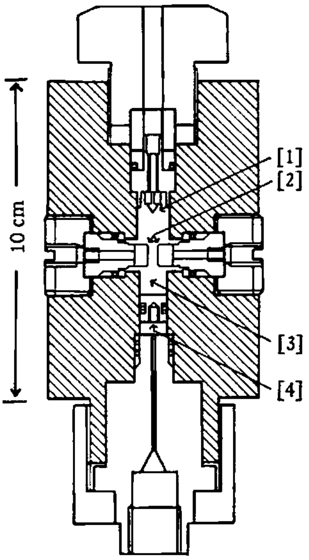

Fig. 2 High-pressure optical cell (D in Fig. 1).
[1]: Thermocouple,
[2]: Sapphire window,
[3]: Sample chamber,
[4]: Piston for separation.

The schematic diagram of the high-pressure apparatus is shown in Fig. 1. The devices A, C, K are fixed by strong steel plates so that they may be aligned on a definite level. The inside of the high-pressure optical cell D is drawn in Fig. 2. The separator [4] has a rubber O-ring so as to prevent the sample from being mixed with the silicone oil used as a pressure-transmitting fluid in E, F, and G. The friction about the O-ring, the difference in pressure between the sample and silicone oil, was measured by means of a manganin coil used instead of a chromel-alumel thermocouple [1] and a calibrated Bourdon gage F. The static friction was 10 bar at most, and the dynamic one when the separator was moving due to the expansion of the heated sample was negligible. Since any amount of thermal expansion of the sample could be absorbed sufficiently by the pressure reservoir E, slow isobaric heating was possible at each pressure. The amplifying recorder J and the thermocouple were calibrated before high pressure runs by using the transition point, 32.38°C of $Na_2SO_4 \cdot 10H_2O$ to Na_2SO_4. The reliability of the whole high-pressure apparatus was tested by measuring the melting point of carbon tetrachloride (Nakarai Chemicals Co., Ltd., guaranteed reagent grade) up to 2 kbar. The result accorded well with those by Amagat33), Bridgman34), and others35). The optical cell was

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33) E. H. Amagat, *Compt. Rend.*, **105**, 165 (1887)

34) P. W. Bridgman, *Phys. Rev.*, 3, 153 (1914)

35) S. D. Hamann, "Physico-chemical Effects of Pressure," Butterworths, London (1957), p. 224

safely employed up to 3.5 kbar at 135°C in a preliminary experiment. By using the above equipment, temperature and pressure were measured to ±0.1°C and ±1 bar, respectively.

About 1-cm^3 sample in the isotropic liquid state was poured into the high-pressure optical cell with a syringe so as to get rid of air inside the cell. The transition temperatures were determined from a drastic change in transparency mainly during the isobaric heating at a rate of 0.2°C min^{-1} or sometimes during the isothermal decompression. The transition temperatures determined thus were reproducible within 0.5°C under the present experimental conditions. Such processes as the isobaric heating and the isothermal decompression were taken to avoid possible supercooling or superpressing, but they were not detected in the mesomorphic transitions studied here.

Results and Discussion

The transparency change for the Ch-IL (T_3) and So-IL (T_4) transitions was clearly detected, while that for the So-Sm (T_1) and Sm-Ch (T_2) transitions was too small to be determined accurately. As shown in Fig. 3, the transition temperatures, T_3 and T_4 are linear against pressure. They are expressed by the following equations;

$$T/°C=75.0+0.025\ (P/\mathrm{bar}), \qquad (1)$$

and

$$T/°C=81.3+0.028\ (P/\mathrm{bar}), \qquad (2)$$

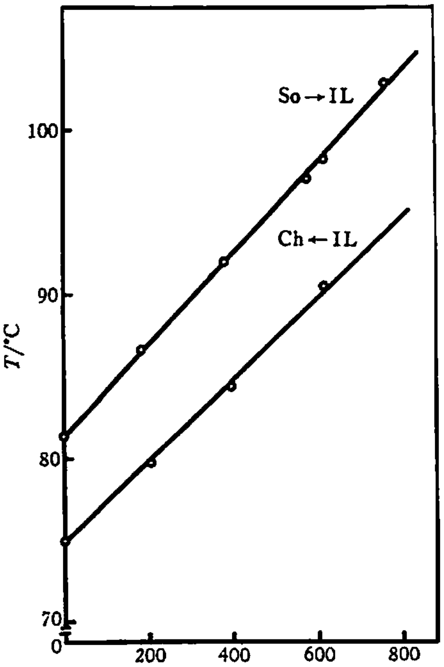


Fig. 3 Pressure dependence of the transition temperatures in cholesteryl stearate.

for the Ch–IL and So–IL transitions, respectively. On the other hand, Semenchenko *et al.* studied this ester volumetrically and reported that

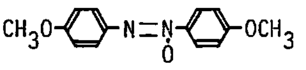
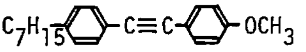
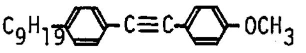
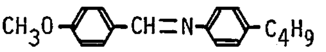
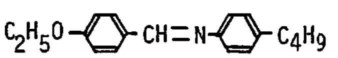
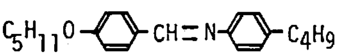
$$T/^{\circ}\mathrm{C}=73.54+0.04759\,(P/\mathrm{bar}), \qquad (3)$$

for "Nematic (Ne)" to "So", and

$$T/^{\circ}\mathrm{C}=77.46+0.03579\,(P/\mathrm{bar}), \qquad (4)$$

for IL to "Ne". It is unusual that the slope for the latter transition is smaller than that for the former. Their transition temperature and slope at 1 bar for Ch–IL disagree with the present, even if their misunderstanding of the phase nomenclature (see Table 1) is corrected from "Ne" and "So" to Ch and Sm, respectively. Under the normal condition, the transition temperatures in this ester have been reported in a number of publications and compared by Davis *et al.*[32] as in Table 1. The discrepancy between the results given by Semenchenko *et al.* and those by the present authors would be ascribed to the difference in the sample purity and that in the method. The sample purity in the present work would resemble that in Davis *et al.*'s in view of the identical transition temperatures and the same purification method. By putting the slopes obtained above, (dT/dP) and the literature values[36] of the enthalpy changes, ΔH (70.5 and 1.64 kcal mol^{-1} for So–IL and Ch–IL, respectively) into Clapeyron's equation, we can obtain the volume changes accompany-

Table 2. The ratio of the volume change for Ch to IL or Nematic to IL to that for So to IL.

Compounds	$(\Delta V_{\mathrm{Ch-IL}}/\Delta V_{\mathrm{So-IL}})\times 100$
cholesteryl stearate	2.2
	$(\Delta V_{\mathrm{Ne-IL}}/\sum \Delta V_i)\times 100$ 3.6[37]
	2.3[38]
	2.8[38]
	3.2[13]
	3.3[13]
	10[3]

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36) G. J. Davis, R. S. Porter, J. W. Steiner, and D. M. Small, *Mol. Cryst. Liq. Cryst.*, **10**, 331 (1970)

37) E. McLaughlin, M. A. Shakespeare, and A. R. Ubbelohde, *Trans. Faraday Soc.*, **60**, 25 (1964)

38) L. Lieber, W. B. Daniels, and J. Billard, *Mol. Cryst. Liq. Cryst.*, **41**, 57 (1977)

ing the phase transitions, ΔV as;

$$\Delta V = \Delta H T^{-1} (dT/dP). \tag{5}$$

The value of $\Delta V_{\mathrm{So\text{-}IL}}$ is 55 $\mathrm{cm^3mol^{-1}}$ and that of $\Delta V_{\mathrm{Ch\text{-}IL}}$ is 1.2 $\mathrm{cm^3mol^{-1}}$ at 1 bar. Thus, the solid to isotropic liquid transition has a much larger volume change than the cholesteric to isotropic liquid transition has. This remarkable difference in the volume change reflects the fact that the increase in the number of the translational freedoms contributes to the volume change much more than that in the number of the rotational freedoms does; the cholesteric state is characterized by the existence of the rotational order and the other freedoms resemble those in the isotropic liquid state. Although the volume change for the Ch-IL transition is small, the transition is not 2nd but 1st order. Thus, the gain or loss of the two rotational freedoms is enough to make the transition 1st order. The ratio of $\Delta V_{\mathrm{Ch\text{-}IL}}$ to $\Delta V_{\mathrm{So\text{-}IL}}$ is compared with that of $\Delta V_{\mathrm{Ne\text{-}IL}}$ to $\sum \Delta V_i (= \Delta V_{\mathrm{So\text{-}Ne}} + \Delta V_{\mathrm{Ne\text{-}IL}} \approx \Delta V_{\mathrm{So\text{-}IL}})$ for other liquid crystalline materials in Table 2. The volume change ratios are found to be in the range of 2 to 4% for most transitions involving cholesteric or nematic mesophases. The cholesteric mesophase is similar to the nematic from the point of view of the volume change. As a matter of fact, it depends just on the optical activity in a component molecule whether the molecular assembly becomes cholesteric or nematic. The small relative volume change, 2 to 4% clearly tells us that the contribution of the rotational freedoms to the overall volume change accompanying the transition from the solid state to the liquid is by far smaller than that of the translational freedom.

The authors wish to express their sincere thanks to Mr. Fujitsugu Amita for fabricating the high-pressure apparatus. The present work was partially supported by a Grant-in-Aid for Scientific Research No. 054148 from the Ministry of Education, Science and Culture.

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