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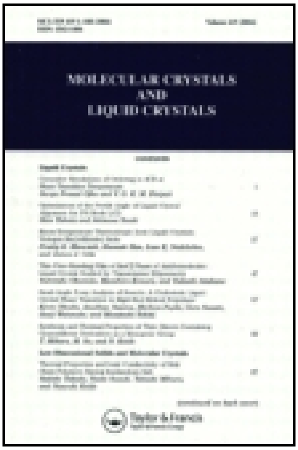

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Optically Determined Mesomorphic Transitions in Cholesteryl Oleyl Carbonate at High Pressure

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Optically Determined Mesomorphic Transitions in Cholesteryl Oleyl Carbonate at High Pressure

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The smectic(S)-cholesteric(C) and cholesteric-isotropic(I) transitions in chromatographically purified cholesteryl oleyl carbonate(COC) have been investigated as a function of pressure(P) up to 3 kbar by an optical method. The transition temperatures(°C) $t_{\text{S-C}}$ and $t_{\text{C-I}}$ are given by the following cubic equations with respect to P(bar): $t_{\text{S-C}} = 22.8 + 0.02087P - 4.70 \times 10^{-7}P^2 - 1.81 \times 10^{-10}P^3$ and $t_{\text{C-I}} = 37.4 + 0.03193P - 5.59 \times 10^{-7}P^2 - 3.49 \times 10^{-10}P^3$. No tricritical behavior of COC is suggested by the present optical observation. Transition entropies $\Delta S_{\text{S-C}}$ and $\Delta S_{\text{C-I}}$ at 1 bar computed by means of Clapeyron's equation are 1.6 and 2.1 J K^{-1} mol^{-1}, respectively.

INTRODUCTION

For the past decade there has been considerable interest in the order of the phase transition from the smectic A(S) to the nematic(N) or to the cholesteric(C) from the viewpoints of both theory and experiment. McMillan's mean-field theory predicts that the S–N (or S–C) transition may become second order under certain conditions.[1] By varying chain length in a homologous series of compounds which form liquid crystalline phases, Doane *et al.*,[2] de Jeu,[3] and Achard *et al.*[4] found that the S–N transition became second order or at least nearly so for sufficiently short molecules. Keyes *et al.*[5] expected that the behavior observed by varying chain length could also be induced for a molecule of a given size through changes in the density with pressure, and reported from their optical observation that the S–C transition in cholesteryl oleyl carbonate(COC) had a tricritical point at 2.66 kbar and 60.3°C. Their finding was followed by Shashidhar and Chandrasekhar; the DTA curves showed that the first-order character of the transition gradually diminished and became prac-

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tically second order at about 2.67 kbar.[6] At the same time, however, they confessed: with the sensitivity of the apparatus, they could not assert unequivocally that the transition was truly second order at such a pressure. Pollmann and Scherer[7] declared a tricritical point in COC at a much lower pressure of 1.43 kbar simply because of a discontinuity of the pressure coefficient of the transition temperature. Recently, Lushington *et al.*[8] examined whether there was a discontinuous break in the enthalpy or entropy at the S–C transition at 1, 1500, and 2625 bar; the heat-capacity peak around the S–C transition was systematically decreased on raising pressure, in qualitative agreement with the DTA result.[6] However, they did not support the reported high-pressure tricritical behavior, stating that the S–C transition in COC might well be continuous even at 1 bar because the existence of a latent heat was uncertain in their curves of the heat capacity vs. temperature. But a recent dilatometric study on a chromatographically purified sample is in favor of the conclusion that the S–C transition is weakly first order at 1 bar.[9] It is well known that the sample purity is of great importance for a detailed study of the phase transition, whereas samples in most high-pressure experiments mentioned above are not so high in purity. A sample purified in the same way as in the previous work[9] is utilized in the present high-pressure experiment. Variation of the intensity of transmitted laser has been measured around the S–C and C–I transitions up to 3 kbar.

EXPERIMENTAL

A sample of COC at high purity was prepared from a reagent-grade one supplied by Tokyo Kasei in the same way as in the previous paper.[9] The S–C transition temperature at 1 bar reflects the degree of purity; its value of 22.8°C is higher than 17,[5] 15,[6] or 13°C[8] but slightly lower than 24°C.[7]

The transition temperatures were determined to ±0.2°C by using an apparatus designed previously; a He–Ne gas laser and a phototransistor were used as a source and a detector, respectively and a calibrated thermocouple (chromel-alumel) was placed in the sample (ca. 1 cm^3) in the high-pressure optical cell. The path length between two sapphire windows was about 5 mm. Pressure was measured to ±1 bar by a Heise Bourdon gage. Details of the high-pressure apparatus and experimental procedure are described elsewhere.[10]

RESULTS AND DISCUSSION

Transparency Variation with Temperature

The transparency of COC varied with temperature in a way similar to that of other cholesteryl esters studied previously.[11] It gradually increased with in-

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creasing temperature within the S and C phases. It dropped once around the S–C transition, forming a "valley" as shown in Figure 1a. The S–C transition temperature was determined from the position where the valley had a bottom. Sometimes, however, two valleys were observed at lower temperatures after a sample was repeatedly compressed and heated. This phenomenon was a sign of depression of the sample purity and led to recovering a white compound which was identified as dicholesteryl carbonate from its melting point (161–163°C) and IR spectrum. As illustrated in Figure 1b, the transparency finally jumped due to the transition from the cholesteric focal conic phase to the cholesteric blue phase.[9] The transition from the cholesteric blue phase to the isotropic phase took place at a temperature higher by 1.1°C at 1 bar. Assuming the small difference was independent of pressure as reported in another case,[12] we obtained the C–I transition temperature at high pressure.

Particular attention is to be focused on the transparency change around the S–C transition because a tricritical point was anticipated at high pressure.[5] The appearance of the valley has been ascribed to strong light scattering and reflection at the boundaries of optically anisotropic domains being vividly reorganized from the smectic order to the cholesteric one.[11] Mobilities of the long molecules, e.g. in the direction normal to the original smectic layer, relates to the rate of the phase transition and therefore, to the shape of the valley.

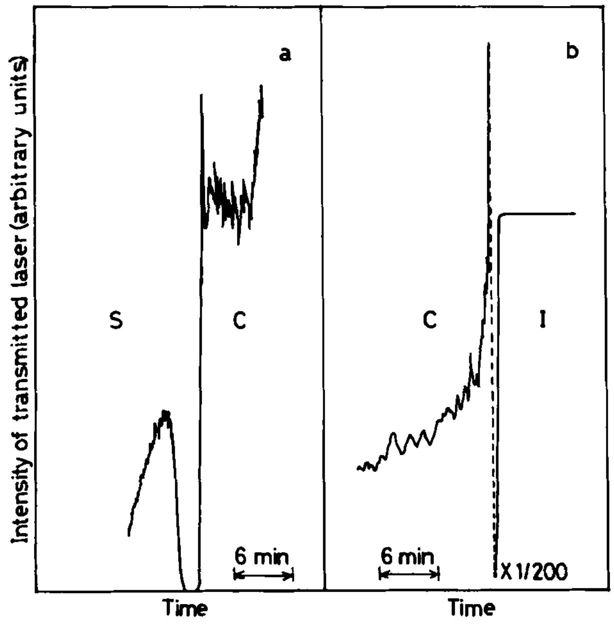

FIGURE 1 Variation of transparency with temperature around the S–C and C–I transitions at atmospheric pressure. Rate of heating is 0.16°C min^{-1} in a and 0.19°C min^{-1} in b. The line after the dashed one is recorded after sensitivity of the detecting system is lowered by the factor (1/200).

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As shown in Figure 2, the width of the valley increases with increasing pressure as a result of decrease in the mobilities; in this case, the heating rates at the high pressures are the same. Cooling experiments were also carried out. The results are qualitatively similar to those shown in Figures 1a and 2, if we record time in the opposite sense. An interesting difference is that the rise in transparency was much slower on cooling than on heating in spite of the same rate of temperature variation; hence, the valley on cooling was several times as wide as that on heating. The lower rate of the transition from the cholesteric to the smectic seems to indicate that there is a large energy barrier for the reorganization of the order from the cholesteric side than from the smectic side. Although the relative intensity of the laser transmitted in the S and C phases (I_S/I_C) was used as a measure to find a tricritical point,[5] it was practically impossible to get a stationary value of I_S after a long interval without the depres-

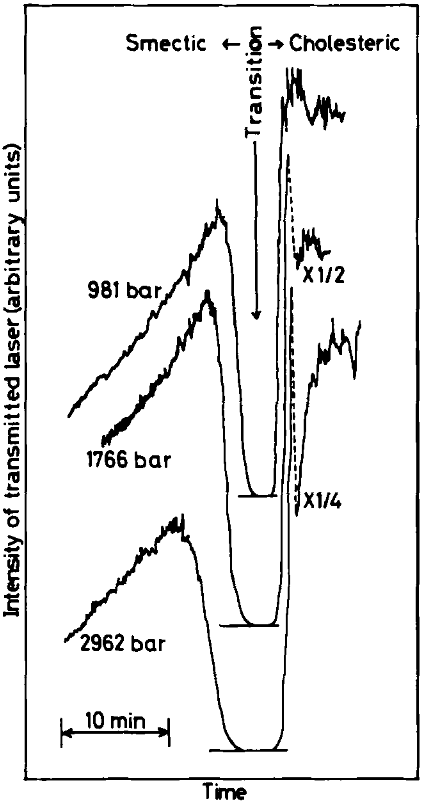

FIGURE 2 Dependence on pressure of transparency change around the S–C transition. Rate of heating is 0.15°C min^{-1} at each pressure. The lines after the dashed ones are recorded after sensitivity of the detecting system is lowered by the indicated factors. The horizontal lines denote zero intensity.

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sion of the sample purity; thus, a question arises concerning validity of the measure (I_S/I_C) for a tricritical point. It does not mean that the present optical method could detect no thermodynamic transition points, because both transition points determined on heating and on cooling agreed well within the experimental uncertainty (±0.2°C), but shows that the light scattering and reflection at domain boundaries depend strongly on the number and size of the smectic domains changing relatively slowly with time under certain conditions. For this reason, I_S at each pressure depend heavily on how temperature and pressure are changed so as to prepare the S phase; thus, it is practically impossible to get high reproducibility of dependence of I_S/I_C on pressure. At any rate, the dependence of the transparency on time or temperature (both variables are linearly related through the constant rate of heating) around the S–C transition is not drastically changed by pressure as depicted in Figure 2, in contrast to the description by Keyes *et al.* Thus, no tricritical behavior of COC is suggested by the present optical study below 3 kbar.

Phase Diagram and Thermodynamic Properties

The phase diagram of COC is shown in Figure 3. At any pressure, the transition points determined in the present work are close to those by Pollmann and Scherer[7] rather than to those by Keyes *et al.*,[5] although results by some others[6,8] are similar to those by Keyes *et al.*; the difference in transition temperatures arises mainly from that in the sample purity and to a less extent from that in the determination method. The phase boundaries in Figure 3 are expressed empirically by the following cubic equations:

$$t = 22.8 + 0.02087P - 4.70 \times 10^{-7}P^2 - 1.81 \times 10^{-10}P^3 \qquad (1)$$

for the S–C boundary with the standard deviation $\sigma = 0.2$°C and

$$t = 37.4 + 0.03193P - 5.59 \times 10^{-7}P^2 - 3.49 \times 10^{-10}P^3 \qquad (2)$$

for the C–I boundary with $\sigma = 0.2$°C, where t(°C) and P(bar) are temperature and pressure, respectively. The transition temperatures $T_{S\text{-}C}$ and $T_{C\text{-}I}$(T in K) and the difference($T_{C\text{-}I} - T_{S\text{-}C}$), which is a kind of measure of stability of the C phase, increase as pressure rises. These trends are common to most liquid crystals. We can not accept the view[7] that the S–C boundary can be divided into two straight lines and their intersecting point be assigned to a tricritical point (1.43 kbar).

An improved version of the mean-field theory for the smectic-A liquid crystal predicts that a second-order transition occurs if the reduced temperature $T_r = T_{S\text{-}C}/T_{C\text{-}I}$ becomes smaller than 0.88 as rod-like molecules get shorter in a homologous series.[13] At high pressure, however, the critical value may be different because the potential parameters, such as δ and ζ_0, would not be inde-

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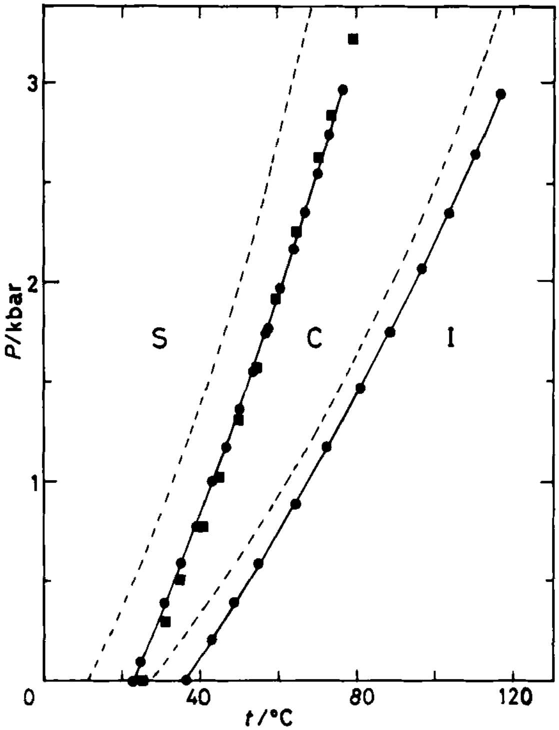

FIGURE 3 Phase diagram of cholesteryl oleyl carbonate. Solid circles are from the present work; solid squares are from Ref. 7; dashed lines are from Ref. 5.

pendent of pressure or density; $T_r = 0.88$ is obtained by using $\delta = 0.65$ and numerous values of the range parameter ζ_0 given by the relation

$$\zeta_0 = 2\pi r_0/d, \tag{3}$$

where r_0 is the range of the intermolecular interaction and d is the spacing of the smectic layers. In the case of COC, there is a tendency that T_r becomes smaller as pressure increases; $T_r = 0.953, 0.926, 0.905$, and 0.892 at 0, 1, 2, and 3 kbar, respectively, according to Eqs. 1 and 2. A second-order transition under the normal conditions is limited to some small value of the layer spacing d according to the theory,[13] and to use this theory for predicting tricritical behavior at high pressure, it is to be known how δ, r_0, d, and other relevant parameters depend on pressure or density. There is a difference in the effect on T_r between an increase in pressure and a decrease in chain length of the molecule; the former elevates both $T_{S\text{-}C}$ and $T_{C\text{-}I}$ but the latter elevates $T_{C\text{-}I}$ and lowers $T_{S\text{-}C}$ as long as the C or N phase exists between the S and I phases.[1,13]

The transition entropy ΔS at 1 bar is calculated from Clapeyron's equation

$$\Delta S = \Delta V (\mathrm{d}T/\mathrm{d}P)^{-1}, \tag{4}$$

where ΔV is the transition volume at 1 bar. When we put the values of $(\mathrm{d}T/\mathrm{d}P)$ from Eqs. 1 and 2 and those of ΔV from Ref. 9 into Eq. 4, we get $\Delta S_{\mathrm{S-C}} = 1.6$ J K^{-1} mol^{-1} and $\Delta S_{\mathrm{C-I}} = 2.1$ J K^{-1} mol^{-1}. Calorimetric studies afford 2.6[14] and 2.1[15] J K^{-1} mol^{-1} as $\Delta S_{\mathrm{S-C}}$ and 2.8[14] J K^{-1} mol^{-1} as $\Delta S_{\mathrm{C-I}}$. The calculated transition entropies are slightly smaller than those directly measured. A theoretical relation between $\Delta S_{\mathrm{S-N(C)}}$ vs. T_r gives $\Delta S_{\mathrm{S-N(C)}} = 1.6$ J K^{-1} mol^{-1} at $T_r = 0.953$ a value of which COC has at 1 bar. Thus, COC has a small but appreciable entropy change at the S–C transition at 1 bar.

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