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A Dilatometric Study of Mesomorphic Transitions in Cholesteryl Oleyl Carbonate and Cholesteryl Oleate

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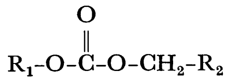
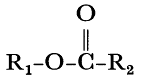
The volumetric behaviors of cholesteryl oleyl carbonate (COC) and cholesteryl oleate(CO) were investigated around the smectic(Sm)-cholesteric(Ch) and cholesteric-isotropic(I) transitions by using chromatographically purified materials. Both transitions showed marked pretransition phenomena in COC and CO. The transition volumes(ΔV) are; for COC $\Delta V_{\text{Sm-Ch}}=0.34$ cm^3 mol^{-1} at 22.8 °C and $\Delta V_{\text{Ch-I}}=0.66$ cm^3 mol^{-1} at 37.5 °C and for CO $\Delta V_{\text{Sm-Ch}}=0.88$ cm^3 mol^{-1} at 45.4 °C and $\Delta V_{\text{Ch-I}}=0.88$ cm^3 mol^{-1} at 50.7 °C. The Sm-Ch and Ch-I transitions are first order as predicted by mean-field theories. The pretransition volume around the Ch-I transition can be treated by the Landau-de Gennes theory for the first-order phase transition.

Compounds which form liquid crystals lose step by step their positional and rotational orders inherent in the crystalline state during successive mesomorphic transitions. Hence, the mesomorphic transition is accompanied by a relatively small volume change. When the mesomorphic transition exhibits a clear discontinuity in volume, of course, it is a first-order transition.[1)] In some cases, however, it is not easy to judge the transition order because a jump in volume is obscured to some extent by pretransition phenomena.[2–10)] There has been considerable interest in the order of the smectic A(Sm) to cholesteric(Ch) transition in cholesteryl oleyl carbonate(COC), which is one of the important compounds commercially utilized for thermal mapping and digital thermometry. A tricritical point was reported in this compound at high pressure first by Keyes *et al.*[11)] and subsequently supported by others,[12,13)] but recently doubted by Lushington *et al.*[14)] Lushington *et al.* stated that there was no clear indication of a discontinuous enthalpy change in their heat capacity-temperature curves at atmospheric and high pressure; they suspected the Sm-Ch transition to be first order at atmospheric pressure, while discontinuous volume[15)] and enthalpy[16)] changes for the transition were reported in unpublished work. Accordingly, it is of great interest to elucidate the detail of the volume behavior of COC at and in the vicinity of the mesomorphic transitions, before arguing the change in the phase-transition order at high pressure.

Cholesteryl oleate(CO) is investigated here to compare the volumetric behavior with COC. They are structurally similar to each other as


$R_1\text{-O-}\overset{\displaystyle O}{\overset{\|}{C}}\text{-O-CH}_2\text{-}R_2$

COC


$R_1\text{-O-}\overset{\displaystyle O}{\overset{\|}{C}}\text{-}R_2$

CO

where R_1 and R_2 are cholesteryl and *cis*-8-heptadecenyl groups, respectively.

Experimental

Materials. Reagent grade COC supplied by Tokyo Kasei was purified by chromatography on a column of silica gel (Nakarai No. III); 1:1 benzene–cyclohexane mixture was used as eluent. The chromatographed COC was recrystallized from acetone, and dried for two weeks in an evacuated desiccator. A thin layer chromatogram of the purified sample (with 1:1 benzene–cyclohexane mixture as eluent) showed two spots; the very strong spot at $R_f=0.70$ was no doubt due to COC and the other weak spot at $R_f=0.82$ was ascribed to dicholesteryl carbonate.[19)] An attempt to remove completely the weak spot resulted in an amount too small to be used in the present precision dilatometry. However, the sample purity would be fairly high because the transition temperatures are close to the most reliable ones[13,20)] in the literature[11,13,14,17–20)] as seen in Table 1. There were another reason why we regarded that the purity was fairly high; crystallization of COC at room temperature was observed only in case of high purity,[20)] and the present sample actually crystallized around 18 °C. After CO was synthesized from cholesterol and oleic acid chloride, it was chromatographed in the same way as in the case of COC and recrystallized from pentanol. The thin layer chromatogram (with 1:1 benzene–cyclohexane mixture as eluent) exhibited only one spot at $R_f=0.71$. Thus, it is easier to purify CO than COC, and as a result, the transition temperatures[8,21,22)] do not scatter so much from one study to another as seen in Table 1.

Apparatus and Procedure. A dilatometer was composed of the two parts connected through a ground-glass joint; a measuring pipet of capillary type and a cell of about 7

Table 1. Comparison of transition temperatures(°C) in COC and CO

Author	C-Sm[a)]	Sm-Ch[a)]	Ch-I[a)]	Method
	COC			
Present	27.0[b)]	22.8	37.5	dilatometry
Gray *et al.*[20)]	26.7	20	34	DTA
Lushington *et al.*[14)]		13.0	35.6	DSC
Pollmann *et al.*[13)]		24	40	optical
Elser *et al.*[19)]		16.3	28	DSC
Adamskii *et al.*[18)]		25	35	optical
Keyes *et al.*[11)]		17	28	optical
Maicachenko[17)]		17	34	?
	CO			
Present	45[b)]	45.4	50.7	dilatometry
Nakahara *et al.*[22)]		43.0	48.5	optical
Armitage *et al.*[8)]	45	46.3	51.3	DSD[c)]
Davis *et al.*[21)]	50.5	42.0	47.5	DSC

a) C, Sm, Ch, and I denote the crystalline, smectic, cholesteric, and isotropic phases, respectively. b) Optical. c) Differential scanning dilatometry.

cm^3. The capillary had a capacity of 0.1 cm^3 and was graduated to 10^{-3} cm^3. The dilatometer was calibrated by using water for which very accurate density data are available at various temperatures.[23] The precision in relative volume change is in the order of 10^{-5}, which is comparable with that in other precision dilatometric studies.[1,7] The purified material was melted and transferred with a syringe to the cell of the dilatometer. The sample in the dilatometer was degassed by repeated melting under vacuum. The whole dilatometer except for the top of the capillary was immersed in a water bath made of glass, so that we could observe color changes accompanying mesomorphic transitions. The well-stirred bath was thermostatted to ±0.01 °C at each temperature. The volume was at first read 15 min after a temperature rise of *ca.* 0.1 °C and every 10 min until it reached a stationary value.

Results

The volume(V/cm^3 g^{-1})-temperature(t/°C) relations of COC and CO in the Sm, Ch, and I phases are shown in Figs. 1 and 2, respectively. The volume varies linearly with temperature except in the ranges where transitions and pretransitions occur. The thermal expansivities are 8.34, 8.31, and 7.68×10^{-4} K^{-1} in the Sm, Ch, and I phases of COC, respectively and 10.32, 9.93, and 7.55×10^{-4} K^{-1} in the Sm, Ch, and I phases of CO, respectively. The trend that the lower-temperature phase has a larger expansivity is often found for liquid crystals.

The volume changes in the vicinity of and at the Sm-Ch and Ch-I transitions are complicated by the pretransition anomalies below and above the transition points, as in other cholesteryl esters,[2-4,6-8] while if the nematic(Ne) phase is involved instead of the Ch phase they are usually much less complicated. These anomalies are relatively more pronounced on the side of the Ch phase. A temperature width of 0.5 °C is required for the Sm-Ch transition to be completed and that of 3 to 4 °C for the Ch-I transition. The transition volume ΔV are defined here by the difference between the two straight lines of the related phases and the transition temperatures by a point where $\partial V/\partial t$ has its maximum value. The transition parameters obtained thus are summarized in Table 2. The transition which has a smaller change in the thermal expansivity, has a smaller change in volume in COC, while such a correlation is not found in CO. The present value of $\Delta V_{\text{Sm-Ch}}$(COC)/cm^3 mol^{-1}, 0.34[24] is slightly smaller than that given by Lorenz and Stegemeyer,[15] 0.411. The value of $\Delta V_{\text{Sm-Ch}}$(CO)/cm^3 mol^{-1}, 0.88 is comparable with that in the literature,[8] 0.92. The value of $\Delta V_{\text{Ch-I}}$(CO), 0.88 cm^3 mol^{-1} is larger than that of $\Delta V_{\text{B-I}}$(CO),[8] 0.49 cm^3 mol^{-1} because the cholesteric to "blue phase" (B) transition is not included in the latter transition volume.[25] The B phase is regarded here as being included in the pretransition phenomena when the volume change for the Ch-I transition is obtained.

When the volume of COC began rising due to the Sm-Ch transition, the turbidity suddenly increased and was followed by a red or scarlet color. In CO, on the other hand, the change in turbidity was less

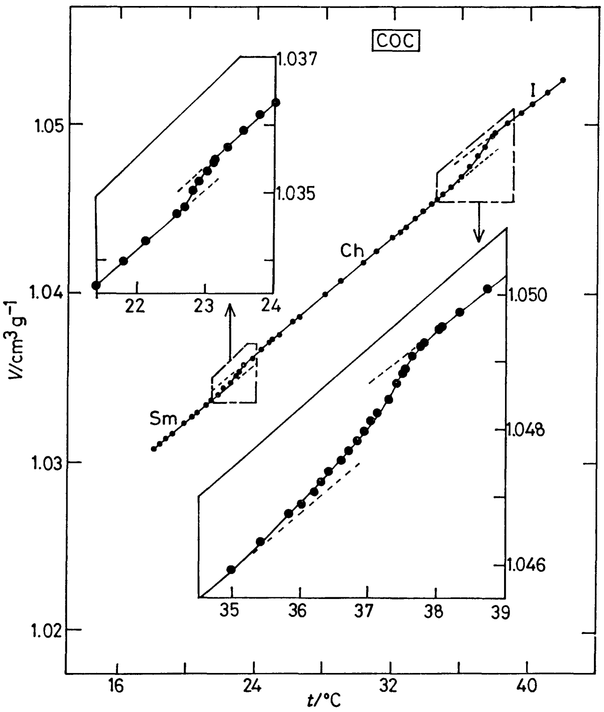


Fig. 1. Volume-temperature relation of COC.

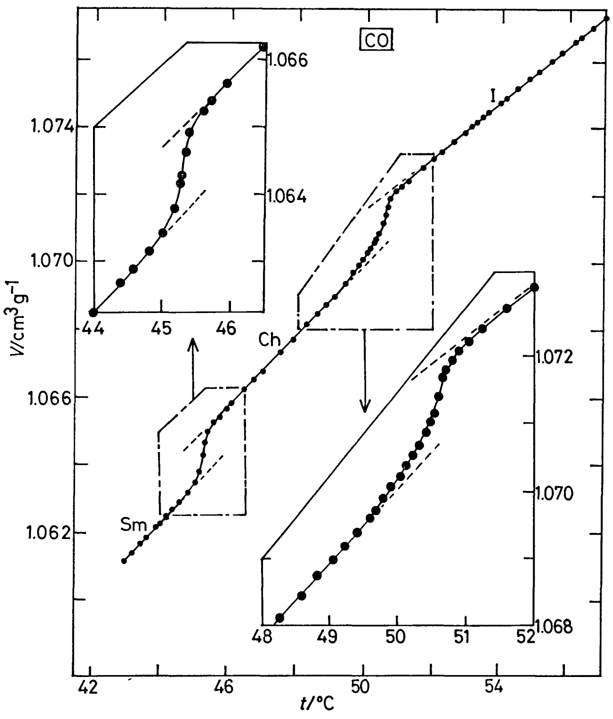


Fig. 2. Volume-temperature relation of CO.

TABLE 2. TRANSITION PARAMETERS FOR COC AND CO

Material	Transition	t_{tr}[a]	ΔV_{tr}[b]
COC	Sm-Ch	22.8	0.34
	Ch-I	37.5	0.66
CO	Sm-Ch	45.4	0.88
	Ch-I	50.7	0.88

a) Transition temperature(°C). b) Transition volume (cm^3 mol^{-1}).

drastic and such a color change did not take place. When the volumes of COC and CO began rising due to the Ch-I transition, a blue color appeared together with a sudden increase in transparency; the point is identified with the Ch-B transition and lower by a few °C than the Ch-I transition point. On cooling, however, the blue color survived until 4 to 5 °C below the point found on heating. Thus, the color change had a hysteresis in contrast to the volume change. On heating, the B phase was seen over the pretransition range below the Ch-I transition point.

Discussion

Sm-Ch Transition. Besides the reasons mentioned in the introduction, there are some theoretical reasons why great attention is paid to the order of the Sm-Ch transition. As well known, the thermodynamic criterion for the first-order transition is simply that the first derivatives of the chemical potential with respect to pressure and temperature become discontinuous at a transition point. As seen in Figs. 1 and 2, it is very difficult to find such a discontinuity in the non-linear portion of the *V-t* relation. The maximum value of $\partial V/\partial t$ is larger in CO than in COC; there is a tendency that the larger the transition volume ΔV the larger the maximum slope $\partial V/\partial t$. The fact that the maximum slope is not infinite but rather small seems to correspond to the finding by Lushington *et al.*[14] that the Sm-Ch peak in the heat capacity-temperature curve is considerably broad and rounded. Thus, it is not easy to decide the transition order solely based on the experimental data; the transition order will be discussed below in view of theory.

Molecular theories based on the mean-field approximation[26-29] indicate that the Sm-Ne transition is allowed to be second order instead of first order for certain values of the potential parameters. McMillan's theory[27] predicts that a second-order transition occurs if the reduced temperature $T_r = T_{\text{Sm-Ne}}/T_{\text{Ne-I}}$ is smaller than $T_r^c = 0.87$; $T_r^c = 0.88$ according to a more refined calculation.[28] The present results in Table 2 give 0.953 and 0.984 as $T_r = T_{\text{Sm-Ch}}/T_{\text{Ch-I}}$ for COC and CO, respectively; similarity in the phase behavior between the Ch and Ne phases is assumed here, as often it is. These values are considerably larger than the critical value of T_r. The difference between T_r and T_r^c is smaller in COC than in CO, corresponding to the relation $\Delta V_{\text{Sm-Ch}}(\text{COC}) < \Delta V_{\text{Sm-Ch}}(\text{CO})$. The order of the Sm-Ne transition in CBOOA[30] has been investigated using several different experimental techniques,[31-36] and most of the experimental results[31-34] except some ones[35,36] are in favor of the first-order transition. The reduced temperature for COC, 0.953 is even larger than that for CBOOA, 0.935. Thus, the Sm-Ch transition in COC is more difficult to become second order than at least that in CBOOA is. The comparison of T_r values supports the conclusion that the Sm-Ch transition in COC is weakly first order at atmospheric pressure. Indeed, there is a theory which predicts that the Sm-Ch(Ne) transition is always at least weakly first order.[37]

Ch-I Transition. It is generally accepted that the Ch(Ne)-I transition is first order. The mean-field theories[26-29,38] indicate that the Ne-I transition is always accompanied by a discontinuous change in the long-range orientational order parameter. Since the Ch phase is similar to the Ne phase as mentioned above, the Ch-I transition is also expected to have a discontinuous change in the order parameter. In practice, however, the *V-t* relations in Figs. 1 and 2 show no clear discontinuity at the Ch-I transition due to the pretransition phenomena, as in the case of the Sm-Ch transition. The volume changes with temperature in the pretransition region of the Ch-I transition are expressed as follows;

$$V = V_{\text{Ch}}^{\text{n}} + 8.7\times10^{-4} - 5.9\times10^{-4}(37.56-t)^{1/2} \qquad (1)$$

$$V_{\text{Ch}}^{\text{n}} = 1.01548 + 8.69\times10^{-4}\,t \qquad (2)$$

for COC and

$$V = V_{\text{Ch}}^{\text{n}} + 8.1\times10^{-4} - 6.7\times10^{-4}(50.53-t)^{1/2} \qquad (3)$$

$$V_{\text{Ch}}^{\text{n}} = 1.01683 + 10.63\times10^{-4}\,t \qquad (4)$$

for CO.[39,40] Here, V_{Ch}^{n} (cm^3 g^{-1}) denotes the normal volume without the pretransition anomalies, and the constants in Eqs. 1 and 3 are determined by the least-squares fitting of $(V-V_{\text{Ch}}^{\text{n}})^2$ to a function, $a(b-t)$ (a and b, constants). Figure 3 illustrates how Eqs. 1 and 3 fit the experimental data. The anomalous (nonlinear) dependence of the volume on temperature below the transition point can be explained in terms of the Landau-de Gennes theory for the first-order transition.[41,42] The Gibbs free energy G is assumed here to be expanded in powers of a scalar order parameter s as

$$G = G_{\text{I}} + (1/2)As^2 - (1/3)Bs^3 + (1/4)Cs^4, \qquad (5)$$

where G_{I} is the free energy of the isotropic phase.[43] Here, as A is often assumed to have the form $A_1(T-T^*)$ in order to discuss the transition thermodynamics, it is expanded here as

$$A = A_1(T-T^*) + A_2(P-P^*). \qquad (6)$$

The coefficients A_1, A_2, B, and C are constants, and T^* and P^* are somewhat below the transition temperature and pressure, respectively. The equilibrium

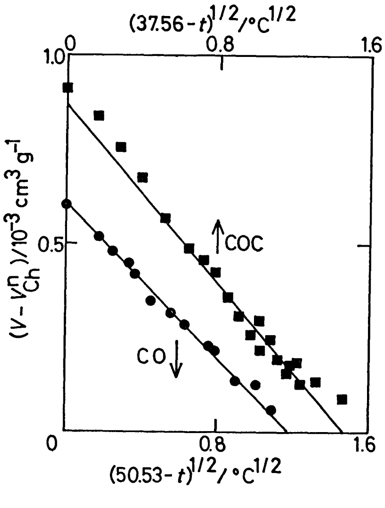


Fig. 3. Fitting of Eqs. 1 and 3 to the pretransition volume data below the Ch-I transition point.

values of s in the Ch phase are obtained as the solutions of the equation $\partial G/\partial s=0$; $s=0$ for the I phase and for the Ch phase

$$A - Bs + Cs^2 = 0. \tag{7}$$

Differentiating Eq. 5 with respect to pressure at constant temperature and taking account of Eqs. 6 and 7, we get

$$\begin{aligned} V = V_{\mathrm{I}} &- A_2B^2/4C^2 + (A_2^2/2C)(P-P^*) \\ &+ (A_1A_2/2C)(T-T^*) - (A_2B/4^{1/2}A_1^{1/2}C^{5/2}) \\ &\times \{[B^2/4A_1C-(A_2/A_1)(P-P^*)]-(T-T^*)\}^{1/2}. \end{aligned} \tag{8}$$

If V_{I} varies linearly with temperature, the equation derived above has the same form as Eqs. 1 and 3 with respect to temperature. If the coefficient B is zero as in the case of the second-order transition, the last term on the right-hand side of Eq. 8 drops, and V becomes a linear function of T. This is not the case, as shown by Eqs. 1 and 3. Thus, the nonlinear behavior of the volume in the pretransition region is explained by the existence of the third term in Eq. 5 which is required for the first-order transition.

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