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Thermoanalytical Microscopy of Phase Transitions of Cholesteryl Acetate-Cholesteryl Octanoate Binary System

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Thermoanalytical Microscopy of Phase Transitions of Cholesteryl Acetate-Cholesteryl Octanoate Binary System

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Cholesteryl acetate-cholesteryl octanoate binary system shows an eutectic point and the eutectic has an enantiotropic cholesteric phase, while both components are monotropic. The phase diagram is discussed with the Schröder-van Laar equation.

The cholesteric flow on cooling behaves as a colloidal state, of which selective light scattering appears periodically.

The once melted solid state is modified to be apparently miscible also in the solid state.

INTRODUCTION

Studies of phase diagrams for mixtures of liquid crystalline materials are given by Gray.[1] Phase transitions of mixture of aliphatic cholesteryl esters were studied by means of differential scanning calorimetry.[2] The study of thermal properties of mixtures of liquid crystalline materials is still important from the standpoints of electronic applications and biological investigations.

In this paper, the phase transition of mixtures of cholesteryl acetate(CA)-cholesteryl octanoate(CO) is studied by means of thermoanalytical microscopy.

EXPERIMENTAL

Samples

CA and CO of Tokyo Kasei Co. were recrystallized twice from *n*-hexane solutions. Melting points of CA and CO after the recrystallization were

TABLE I

Notations of the binary samples

Samples	Mole fraction of CA
B 1	0.050
B 2	0.159
B 3	0.283
B 4	0.404
B 5	0.500
B 6	0.569
B 7	0.655
B 8	0.730
B 9	0.863
B 10	0.950

387.2 ± 0.5 K and 381.2 ± 0.5 K respectively. The X-ray diffraction patterns of both crystals deposited from the *n*-hexane solutions coincide with those of the crystals obtained from the ethanol solutions respectively.

In order to avoid the first thermal history of samples, the mixtures were not made by fusion but by well pestling both components in an agate mortar. Table I gives the notations of the mixture samples.

Thermoanalytical microscopy (TAM)

The apparatus employed, reflex-type, was reported elsewhere.[3] Microscopy was carried out by magnification 100 through crossed polars.

RESULT

The binary system shows an eutectic and an enantiotropic mesophase, while both components are monotropic. Figure 1† shows an example of TAM of sample B4. The excess CO crystals which appear in photos. 7–10 grow from the cholesteric phase over the eutectic point (cf. Figure 12). Solidification peak does not appear due to supercooling. Photograph 15, taken on the next day, shows the solid state which is very similar to the cholesteric phase.

Figure 2 shows the transition temperatures obtained by TAM for all samples. The temperatures determined are the peak points, not the onset points, since the peaks cover very wide temperature ranges except for the chol.-iso. transitions. Each point expresses the mean value of a few samplings of the composition. In the lines of co-existence of crystals and solution, the

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† The polymorphic transition of CA on first run[7] is suppressed by the broad eutectic peak.

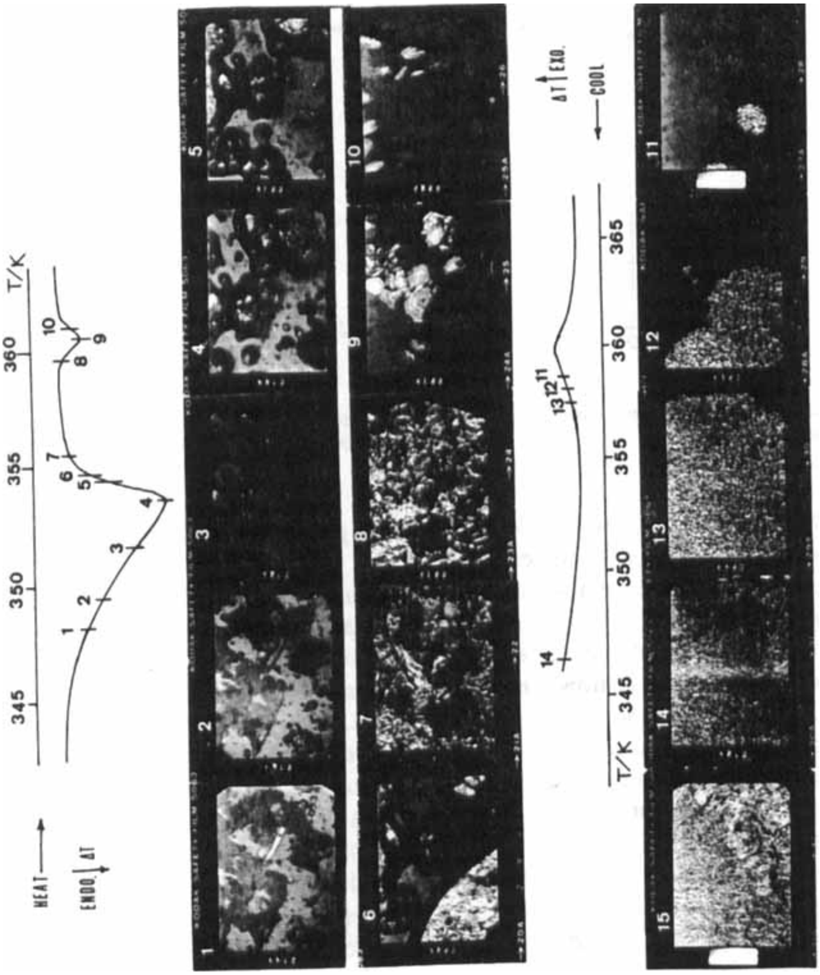


FIGURE 1 Thermoanalytical microscopy of cholesteryl acetate-cholesteryl octanoate binary mixtures. Mole fraction of CA, 0.404; sample weight, 5.76 mg; scanning rate, 2.5 K/min; chart speed, 20 mm/min.

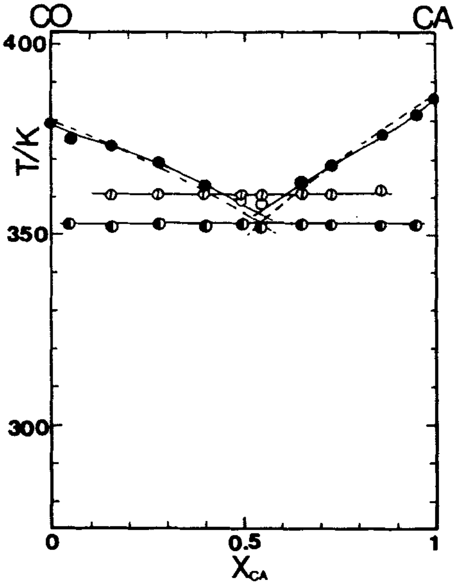


FIGURE 2 The transition temperatures of CA-CO system on heating. ◐—Eutectic point; ⦶—chol.-iso. transition point; ○—melting point of excess component; ●—reproducible melting point of excess component on second heating.

black circles express identification of the fusion peak, while the white circles, no peak but only fine crystals remained.

Figure 3 shows the transition temperatures on cooling. The freezing points in the middle range of compositions are not obtained owing to supercooling. The color variation of the cholesteric phase on cooling was studied under reflected light. Figure 4 shows the situation regarding B6 (sample thickness, ca. 0.5 mm, no cover) with the scanning rate, 2.5 K/min. Photograph 0 was taken at an instance of the chol.-iso. transition on heating. Photograph 1 to the end were taken on cooling. With the appearance of iso.-chol. transition peak, light scattering starts from purple and changes into yellow (No. 1) and successively to dark (No. 2), although photography failed to catch the purple. After those variations, the view changes into bright yellow (No. 3) and changes to blue with reddish clusters (No. 4). Afterwards, the clusters grow like seaweeds on cooling (No. 8) and sometimes disperse instantaneously by Brownian motions (No. 9). The color variations shift from a short wave length's color to a longer wave's one by the dispersion of these clusters into the previously homogenized phase.

In the compositional extremes, such as B1 or B9, the eutectic peak succeeds to the freezing peak of the excess component in the DTA, irrespective of the temperature expected (Figure 5).

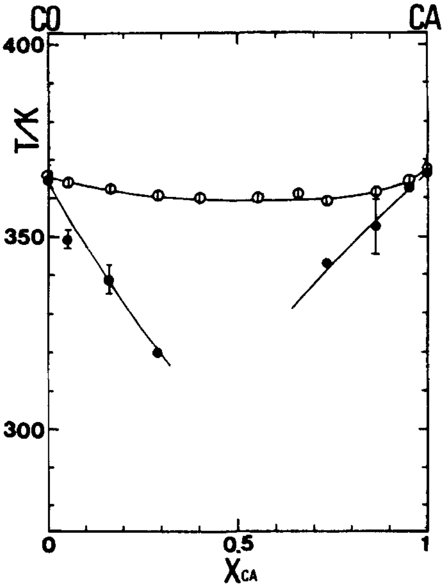


FIGURE 3 The transition temperatures of CA–CO system on cooling. ⦶—Chol.-iso. transition point; ●—Freezing point.

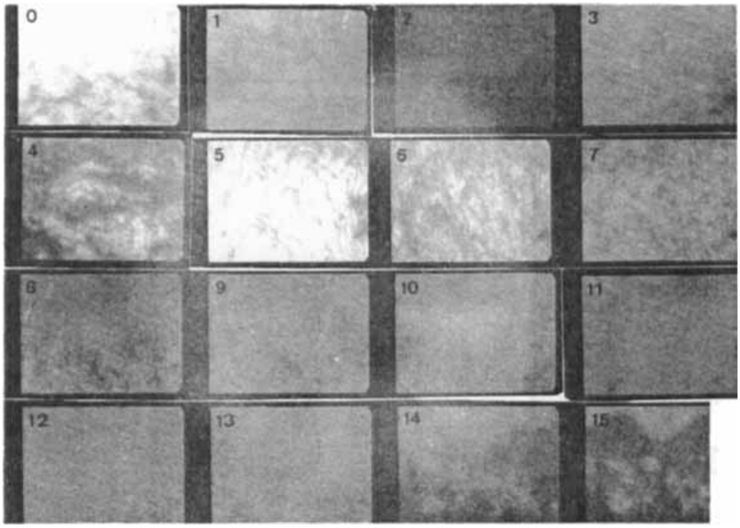


FIGURE 4 Color variation of the cholesteric phase of CA–CO mixture. Sample: B6. Temperatures for photos. 0—357.9 K; 1—360.2 K; 2—359.5 K; 3—355.8 K; 4—352.0 K; 5—346.5 K; 6—343.0 K; 7—338.9 K; 8—335.1 K; 9—332.7 K; 10—331.7 K; 11—322.7 K; 12—319.5 K; 13—311.2 K; 14—308.6 K; 15—308.2 K.

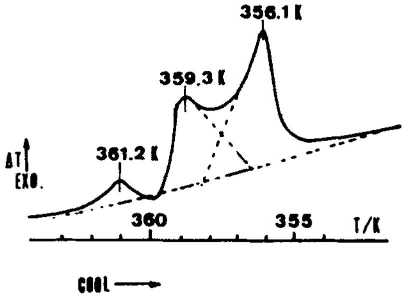


FIGURE 5 Cooling curve of sample B9 (x_{CA} = 0.863).

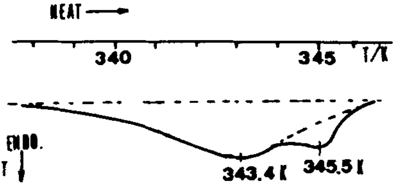


FIGURE 6 Eutectic peak of sample B4 (x_{CA} = 0.404) on second heating.

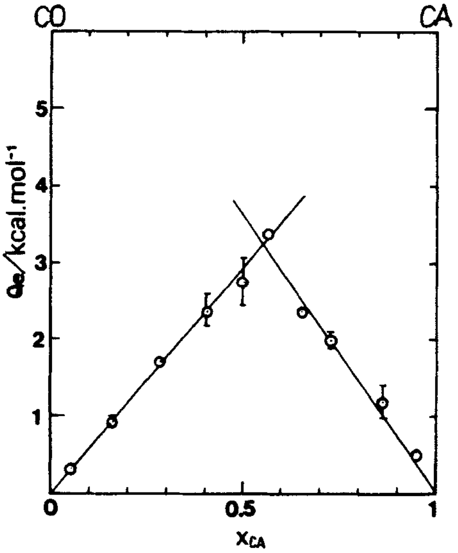


FIGURE 7 Eutectic heat and composition.

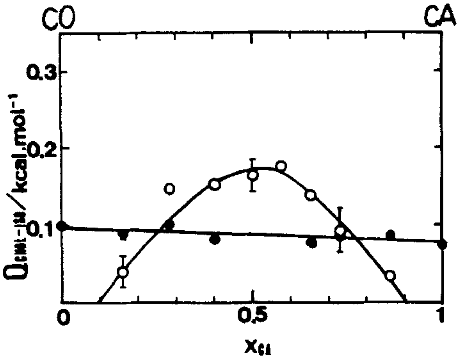


FIGURE 8 Heat of chol.-iso. transition and composition. ○—on heating; ●—on cooling.

Second scannings give the broader and more ambiguous peaks except chol.-iso transition. In the medial range of composition, such as B4, B5 or B6, two peaks superpose around the eutectic point (several degrees lower than that of first run) as shown in Figure 6.

Eutectic heat and the heat of chol.-iso. transition were estimated (Figures 7 and 8). Mean molecular weight is employed for both estimations.

DISCUSSIONS

Although the formation of an enantiotropic mesophase from a mixture of monotropic substances is not a surprizing result as indicated by Gray,[1] the following items should be discussed:

1 Theoretical eutectic point

In the binary system of components, 1 and 2, the Schröder-van Laar equation,

$$-\ln x_i^1 = \frac{\Delta_f H_i^0}{R}\left(\frac{1}{T} - \frac{1}{T_i^0}\right) \tag{1}$$

where x_i^1, mol fraction of component $i (i = 1 \text{ and } 2)$ in the solution

$\Delta_f H_i^0$, the latent heat of fusion of pure component i at temperature T

T_i^0, the melting point of pure component i

R, gas constant,

holds on the following assumptions. Namely, 1 and 2 make an ideal solution, but completely immiscible in the solid state, the latent heat should be independent of temperature, and the difference between the specific heats of the liquid and solid must be negligibly small.

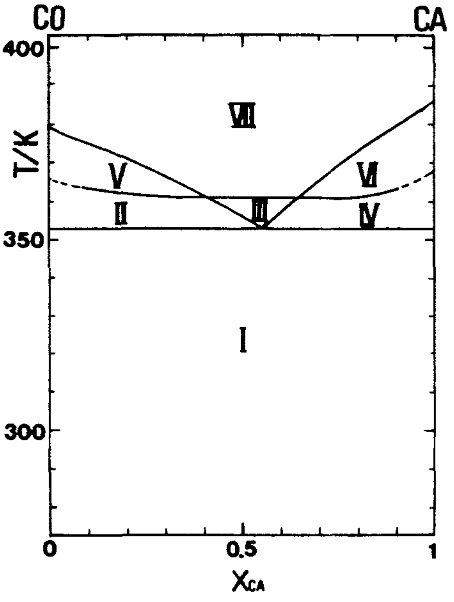


FIGURE 9 Phase diagram of CA–CO binary system. I—CA crystals and CO crystals; II—Cholesteric phase and CO crystals; III—Cholesteric phase; IV—Cholesteric phase and CA crystals; V—Isotropic melt and CO crystals; VI—Isotropic melt and CA crystals; VII—Isotropic melt.

The latent heats of fusion of CA and CO are 4.80 Kcal/mol and 7.13 Kcal/mol respectively. The theoretical curves (slashed lines in Figure 2) obtained from these values in Eq. (1) give an intersecting point, $x_{CA} = 0.54$, $T_e = 353.2$ K which is identical with the empirical eutectic point. The coincidence proves that the assumptions of Eq. (1) hold in this system.

The phase diagram can be drawn as shown in Figure 9, taking account of Gibb's phase rule.

2 Curvature of co-existing curves of crystals and solution[4]

The curvatures of the empirical lines of co-existence of crystals and solution are concave, while those of the theoreticals are convex, at the compositional extremes.

Eq. (1) can be expressed in the form,

$$T = \frac{\Delta_f H_i^0}{R} \frac{1}{\left(\dfrac{\Delta_f H_i^0}{RT_i^0} - \ln x_i\right)} \qquad (2)$$

Thus,

$$\frac{\partial^2 T}{\partial x_i^2} = \frac{\Delta_f H_i^0}{R} \frac{1}{\left(\dfrac{\Delta_f H_i^0}{RT_i^0} - \ln x_i\right)^2} \left\{ \frac{2}{\dfrac{\Delta_f H_i^0}{RT_i^0} - \ln x_i} - 1 \right\} \frac{1}{x_i^2} \tag{3}$$

The sign of this derivatives, which gives the curvature of the line of co-existence of crystals and solution, depends upon the following condition,

$$\frac{\Delta_f H_i^0}{RT_i^0} - \ln x_i \gtrless 2 \tag{4}$$

At the compositional extremes, $\ln x_i \risingdotseq 0$. Therefore, in the region, $x_i \rightarrow 1$, if

$$\frac{\Delta_f H_i^0}{RT_i^0} > 2, \quad \frac{\partial^2 T}{\partial x_i^2} < 0 \tag{5}$$

and,

$$\frac{\Delta_f H_i^0}{RT_i^0} < 2, \quad \frac{\partial^2 T}{\partial x_i^2} > 0 \tag{6}$$

Eqs. (5) and (6) suggest the entropy of fusion of the predominant component controls the curvature. A few cases holding Eq. (6) are known. Those are the cases that the solvent molecules are spherical, such as tetramethylsilane, or associated, such as cyclohexanol.[4]

The entropies of fusion of CA and CO are 12.4 cal/mol. K and 18.7 cal/mol. K respectively. Then they correspond to the common case, Eq. (5). The discrepancy might be owing to the special arrangement in the mesophase. The curvature of the chol.-iso. transition line is also positive at the compositional extremes, though assumption of ideal solution claims the complete linearity in the full range of composition.

3 Eutectic heat and chol.-iso. transition heat

Eutectic heat (Figure 7) has the maximum value at around $x_{CA} = 0.55$, nearly equal to the theoretical triple point, 0.54.

The chol.-iso. transition heat (Figure 8) on heating also shows maximum at a middle composition. The corresponding heat on cooling roughly fits on a straight line, proportional to composition. That is, the cholesteric phase on heating belongs to the eutectic mixture of which amount changes with composition.

4 Cholesteric phase on cooling

The difficulty of crystallization in the medial range of composition prolongs the cholesteric phase down to room temperature. The cholesteric flow in

Figure 4 is reminiscent of a colloidal solution. Since the co-mesophase must be homogeneous from the above discussion, the colloidal state must have a homogeneous composition of both components. The repetition of color appearances (Photographs 1–4) seems difficult to explain in terms of the so called pitch theory. The repetition was also observed in a previous work.[5] The color variation appears to reflect the degree of crystal growth of anisotropic colloidal particles in the mesophase. In cholesteric phase, the concept of "COLLOID" particularly gives rise to an imagination of opticalactive particles of which size equals to the nominal pitch of the helical structure. Basing on our observations, the repetition of same color appearance suggests the growth of the particle size as well as the higher order reflections of Bragg scattering. Namely, the repetition means $m > 1$ in the equation,

$$2s = p = m\lambda,$$

where s is the size of particles, p is the pitch of the helical structure, m is integer, and λ is the selective wave length of incident light beam, satisfying Bragg reflection. According to de Gennes,[6] all orders of the reflections are observed in the case of oblique incidence. In a thick sample, all oblique incidences of light beam may be possible.

5 Melt crystallized mixtures

Ambiguous broader curves on second scannings suggest that the frozen states have a considerable amount of lattice defects. Figure 10 shows the X-ray (Cu Kα, Ni-filtered) diffraction patterns of the mixtures. Group A is the pattern of the original blend samples, while B is that of 3 days after heat treatment, holding an hour at 403 K. The large difference between A and B is due to the transformation of once melted CA.[7] Besides the difference, there is a notable difference between A and B, that is, the position of each line of group A does not shift from the original position of each pure component, while each line of group B subtly shifts depending on composition. The impurities of B5 determined by gas chromatography before and after treatment are 0.6 % and 3.0 % respectively. Any new spacings do not appear in group B excepting the slight shifts. The situation implies a modified structure including the lattice defects as the intermediate sites. Impurity levels of 2.4 % due to decomposition may also take a part of the lattice imperfection.

Figure 11 shows the spherulitic solid states of B3 and B8 produced by the same treatment as that of X-ray samples. It suggests that immiscible crystals can still form a spherulitic structure. Figure 12 shows the situation of reheating of sample B8 with 0.3 K/min, after cooling with 2.5 K/min. The spherulitic structure (No. 1) disappears gradually (No. 2) and a sludgy state holds up to the eutectic point (No. 3). The excess CA crystals grow gradually between

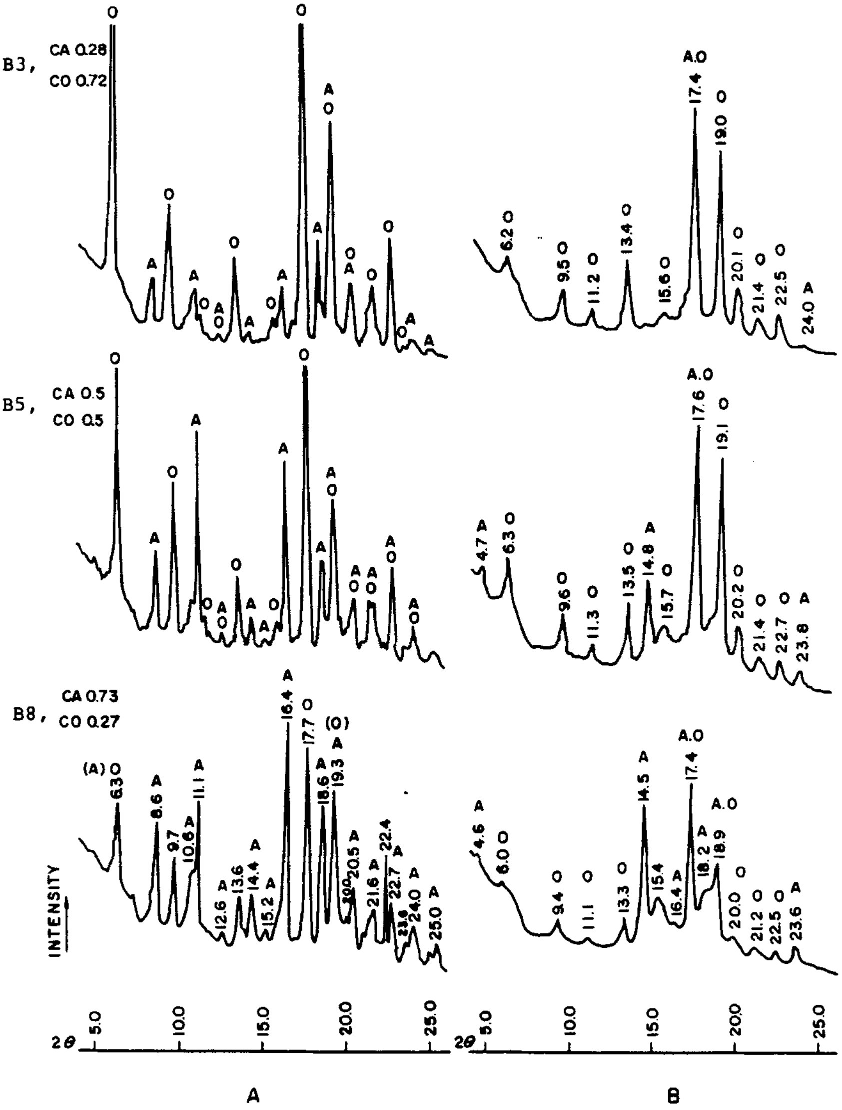
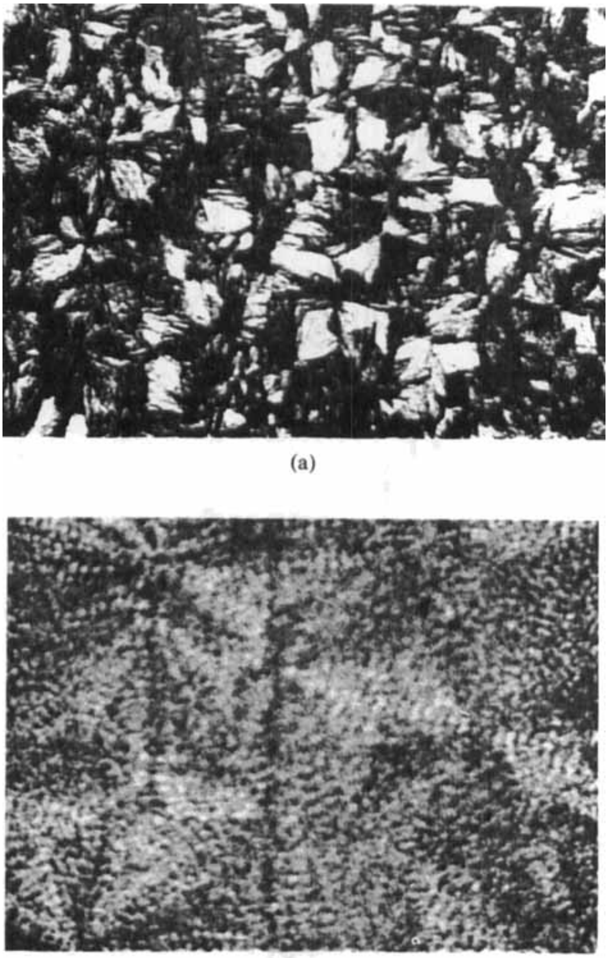


FIGURE 10 X-ray diffraction patterns of the mixtures. Group A—Original blend samples; Group B—The same samples 3 days after heat treatment.



(a)

(b)

FIGURE 11 Spherulitic solid states of frozen mixtures. A—B3 (x_{CA} = 0.283), B—B8 (x_{CA} = 0.730).

the eutectic point and the chol.-iso. transition point (No. 4–6) over which only the CA crystals are remained (No. 7) and dissolved again with temperature (No. 8).

Our data indicates melt crystallized mixtures are similar to solid solution in the medial range of composition. Considered together with the results of X-ray and microscopy, the solid state might be called as super lattice of higher order.

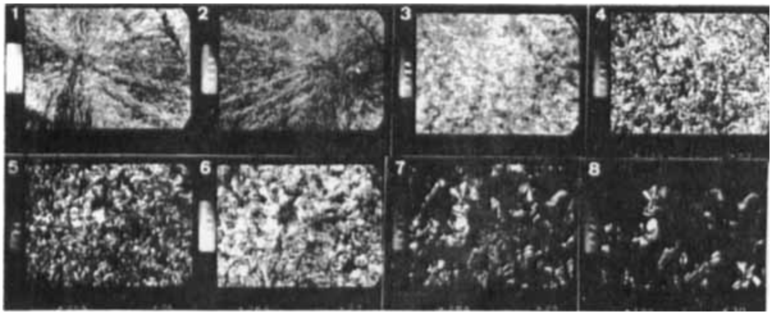


FIGURE 12 Reheating of spherulitic solid (B8), 0.3 K/min. 1—295.1 K; 2—310.6 K; 3—353.0 K; 4—357.3 K; 5—358.3 K; 6—361.4 K; 7—364.4 K; 8—365.2 K.

CONCLUSION

As the conclusion, binary system of cholesteryl acetate-cholesteryl octanoate forms an eutectic which has an enantiotropic cholesteric phase. Although the system follows the Schröder-van Laar equation, the once melted solid state is modified to be apparently miscible also in the solid state by the production of lattice disorder.

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