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Phase Studies on Binary Systems of Cholesteryl Esters[†]

A. Two Aliphatic Ester Pairs

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Abstract—Binary blends for two pairs of esters of cholesterol, the myristate plus acetate and the myristate plus the nonanoate have been characterized to determine the equilibrium phase conditions for the isotropic liquid, the cholesteric and smectic mesophases, and the stable crystals. The phase diagrams were determined using a Differential Scanning Calorimeter (DSC–1B), which also provided the heats of transition. For the more complicated acetate system, morphology was also studied with a polarizing microscope plus hot stage and structure determinations were made using X-ray diffraction.

Results indicate that both ester pairs form a single eutectic mixture. The crystal melting points of the pure components in both pairs follow the van't Hoff equation for melting point depression due to impurity over most of the composition range. A homogeneous cholesteric mesophase was formed in both pairs. The temperatures and heats of the smectic–cholesteric transition for the acetate blend decrease as the concentration of the myristate ester is decreased. Indeed the smectic mesophase was not observed below 78% myristate. Monotropic behavior seriously limits the study of high acetate content blends.

In the nonanoate systems the cholesteric and smectic mesophases exist over the full composition range. This ester pair forms virtually ideal comesophases. Transition temperatures and heats agree well with the theoretical results based on a model which involves ester separation only at the lowest (crystalline solid) transition. The results suggest methods of predicting phase diagrams for other binary mesophase systems.

1. Introduction

Liquid crystals exhibit some of the flow and drop-formation properties of liquids as well as some of the anisotropy, optical and electrical properties of crystalline materials.(1,2) Their multiple transitions are

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characterized by discontinuous changes in physical properties such as density, specific heat and viscosity. Within mesophase classes there can also be additional variations in texture. Many liquid crystals are also monotropic, which means that the mesophase is observed only on cooling; that is, when the transition to the solid state is depressed or supercooled. Mesophase transitions, however, are generally reversible without significant depression on cooling.

The cholesteric mesophase exists almost exclusively in derivatives of cholesterol. Many studies have been made on the homologous series of its aliphatic esters, especially on transition heats and temperatures.(1,3,4) The smectic mesophase has not been generally observed in the lower members of this series; the smectic–cholesteric transition appears distinctly in the *n*-octanoate ester and in higher esters to at least the eicosanoate. The transitions for some of the esters are monotropic for both the cholesteric and smectic mesophases, some are monotropic for the smectic mesophases, and just three pure esters, the tridecanoate, myristate, and pentadecanoate (C_{13}–C_{15}) esters are established as enantiotropic (reversible) for all three transitions.(5)

Few studies have been developed on multicomponent systems of liquid crystals;(1,5–14) none has been reported on the esters of cholesterol prior to studies in this lab.(15) Of particular interest is the effect of composition on the temperature range for the cholesteric mesophase. This type of liquid crystal is used in technological applications because of its thermochromic properties. Cholesterol derivatives are also implicated in coronary disease by their appearance in arteriosclerotic deposits.

For these studies, cholesteryl myristate was chosen as the base component for the binary systems. It is perhaps the most widely studied ester; it is also one of the three esters with three reversible transitions. Cholesteryl acetate was selected as one of the co-components because it possesses the cholesteric (steroid) structure and a short ester tail. The nonanoate was chosen because it has both a structure and molecular weight similar to the myristate ester.

Characterization in this study has involved principally a differential scanning calorimeter (DSC) to determine the transition temperatures and heats for the binary mixtures. Morphology determinations using a polarizing microscope with a Mettler hot stage and structural data from X-ray diffraction were obtained on the more complicated acetate system.

The enantiotropic transition temperatures for relatively pure, ≥ 98 mole %,⁽¹⁶⁾ cholesteryl myristate ester are as follows:⁽³,⁴⁾

$$\text{Solid} \xleftrightarrow{70.5^\circ\text{C}} \begin{matrix}\text{Smectic}\\ \text{mesophase}\end{matrix} \xleftrightarrow{77.8^\circ\text{C}} \begin{matrix}\text{Cholesteric}\\ \text{mesophase}\end{matrix} \xleftrightarrow{83.2^\circ\text{C}} \begin{matrix}\text{Isotropic}\\ \text{liquid}\end{matrix}$$

The cholesteric–isotropic liquid transition temperature for 99.4% cholesteryl acetate determined reported at 94.5 °C;⁽¹⁾ it is difficult to reproduce in pure material due to the rapid formation of the crystals (little supercooling). The transition temperatures for the nonanoate ester have been previously reported.⁽⁴⁾

The corresponding heats of transition are as follows:⁽⁴⁾

Cholesteryl myristate	cal/g
Solid–smectic	18.6
Smectic–cholesteric	0.56
Cholesteric–isotropic liquid	0.41
Cholesteryl acetate	
Solid–isotropic liquid	11.4
Isotropic liquid–cholesteric	0.60
Cholesteryl nonanoate	
Solid–cholesteric	11.4
Cholesteric–isotropic	0.25

The phase diagrams were established from published transition temperatures for the pure components and from new data determined on up to ten blends from DSC data.

Interpretation included application of the Gibbs Phase Rule,

$$f = c - p + 2 \qquad (1)$$

where f is the degrees of freedom for the system, p is the number of phases, and c is the number of components.

The van't Hoff equation was also used:

$$\ln N_1 = -\Delta H(T_0 - T_m)/RT_0T_m \qquad (2)$$

where N_1 is the mole fraction of the major component, T_0 is the melting point of the pure component, T_m is the melting point of the mixture (both in °K), R the gas constant, 1.987 cal deg^{-1} mole^{-1}, and ΔH the molar transition heat of the major component.

2. Experimental

Samples

The esters were obtained from Eastman Kodak Company, Rochester, New York. Recrystallization from *n*-pentanol(3) was used to obtain nonanoate and myristate in $\geqslant 98$ mole % purity. The purity was determined from the shape of the DSC trace(16) and represents a lower limit. The acetate was over 98% as received and was used directly. Ester purity was considered critical only in the compositional extremes.

The blends were prepared in one gram quantities, weighing to 0.001 mg. Blends were heated in air until both esters had melted, stirred with a spatula while molten for complete mixing, and then cooled. For the more complex acetate system, the following blends were used; the compositions are normalized to reflect only the pure myristate and acetate esters:

Cholesteryl Ester Blends
Acetate–Myristate

Myristate mole percent	Acetate mole percent
97.0	3.0
94.2	5.8
91.4	8.6
78.1	21.9
68.4	31.6
54.0	46.0
43.3	56.7
31.9	68.1
18.3	81.7
7.6	92.4

Calorimetry

I. Temperatures

A Differential Scanning Calorimeter, Model DSC–1B (Perkin–Elmer Corporation, Norwalk, Connecticut) was used to determine the transition temperatures and heats. The samples were 2 to 3 mg, measured to 0.001 mg, and sealed in aluminum planchets. The maximum temperature scan was from 0–120 °C (for the pure acetate). The scanning rate for most runs was 2.5 °C per minute. The DSC sensitivity was 0.1 to 0.8 mcal/sec/in and the chart speed was one inch per minute for most runs. Indium and four pure organic standards (*p*-nitrotoluene, stearic acid, naphthalene, and benzoic acid) were used to calibrate transition temperatures and heats. The method of least squares was used to fit the observed and absolute temperatures to a linear curve which, in the range of test temperatures, gave corrected readings accurate to ± 0.6 °C.

II. Heats

The average correction factor for transition heats was 1.05, 1.05, and 1.04 for scanning rates of 1.25, 2.5 and 5.0 °C per minute, respectively. These were determined using indium, naphthalene and benzoic acid. Transition heats were determined by measuring the areas under the transition peaks with a planimeter (Gellman Instruments, Germany). Multiple peaks were commonly observed corresponding to the melting of the eutectic composition followed by melting of the pure second component. To determine these heats, areas were arbitrarily divided by extending a line from the base line at the eutectic temperature to the slope of the second peak. The remaining area was assigned to the eutectic.

III. Heating Rates

Three binary acetate compositions were run in the DSC to determine the effect of heating on transition temperature. The compositions were 97.8, 94.2 and 78.1 mole % myristate and the heating rates were 1.25, 2.5, 5.0 and 10 °C per minute. Figures 1 and 2 illustrate the results by composition showing both heating and cooling studies for each transition. Figure 1 illustrates supercooling of the excess myristate. Figure 2 shows the heating rate effect on the eutectic transition. The results were similar on the 94.2% myristate intermediate concentration. The data were linear, exclusive of supercooling, and were readily extrapolated to the intercept for the theoretical equilibrium transition temperature at zero heating rate. Temperatures for both mesophase transitions on cooling are only slightly depressed—partly due to instrument response—a characteristic that has been detailed by Ennulate,(17) whereas the smectic–solid transitions were supercooled from 20 to 70 °C depending on cooling rate and composition.

Temperatures for establishing the phase diagrams were taken

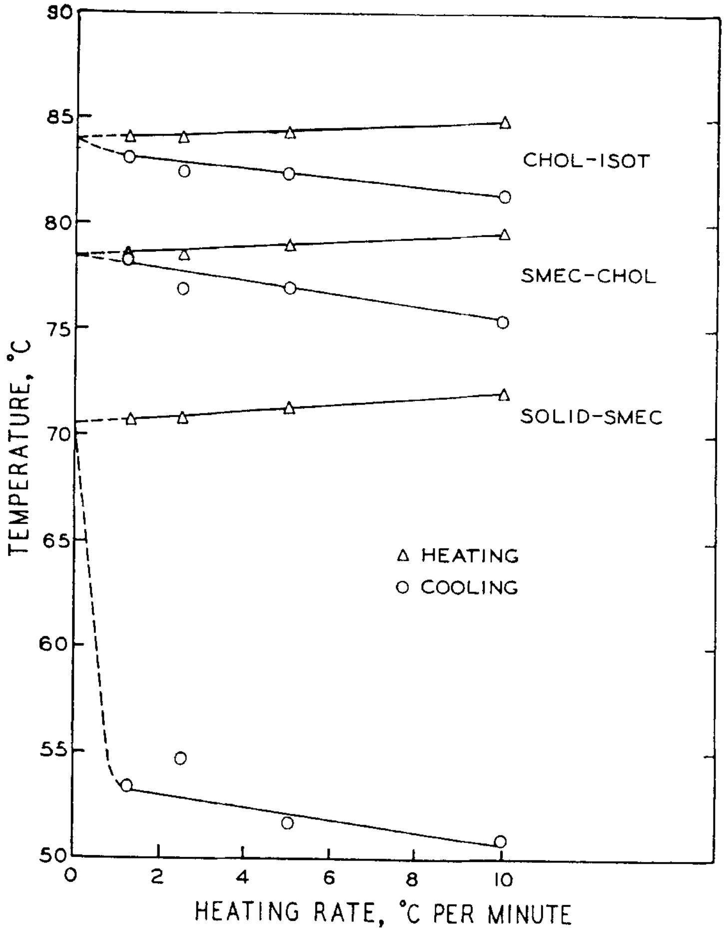

Figure 1. Phase transition temperature vs. heating and cooling rate in DSC—97.8% cholesteryl myristate.

from heating cycles except for monotropic mesophase transitions. In these cases, the isotropic liquid was cooled below the mesophase transition temperature and then heated to observe the transition on heating. The smectic–cholesteric transition was depressed several degrees for the 94.2% cholesteryl myristate blend with acetate whereas for the 78.1% myristate blend, this transition was not readily observed due to its very low heat.

All of the heating rate tests are plotted in Fig. 3 to illustrate the

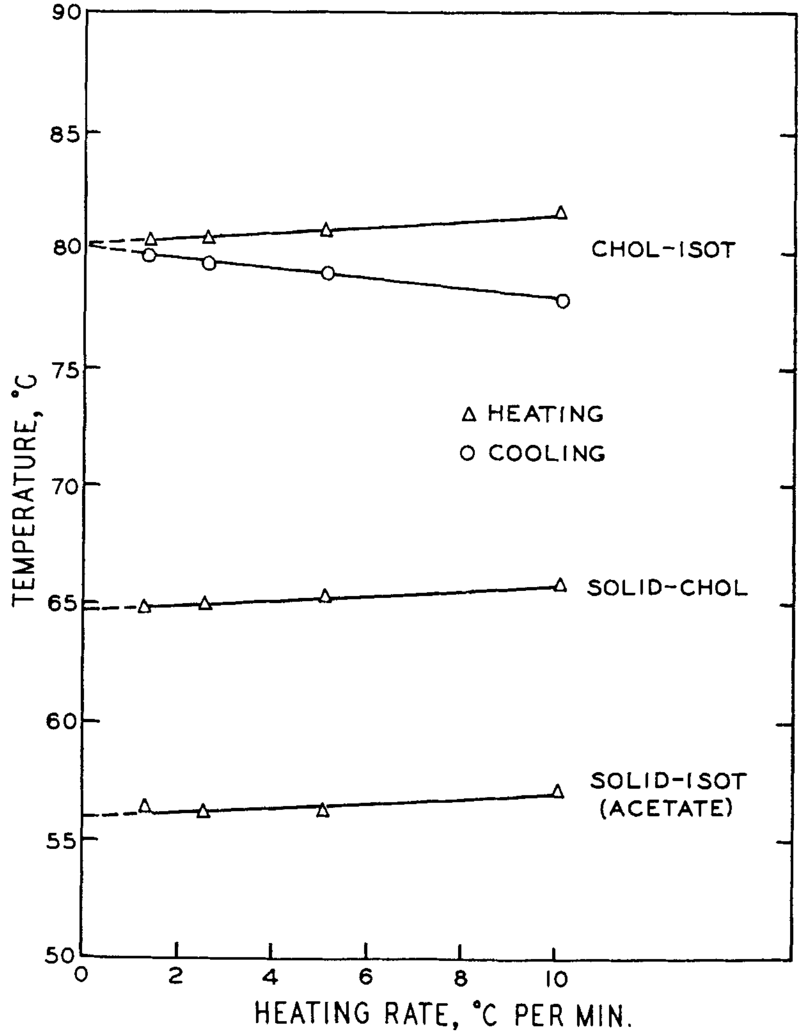

Figure 2. Phase transition temperature vs. heating and cooling rate—78.1% cholesteryl myristate; 21.9% cholesteryl acetate.

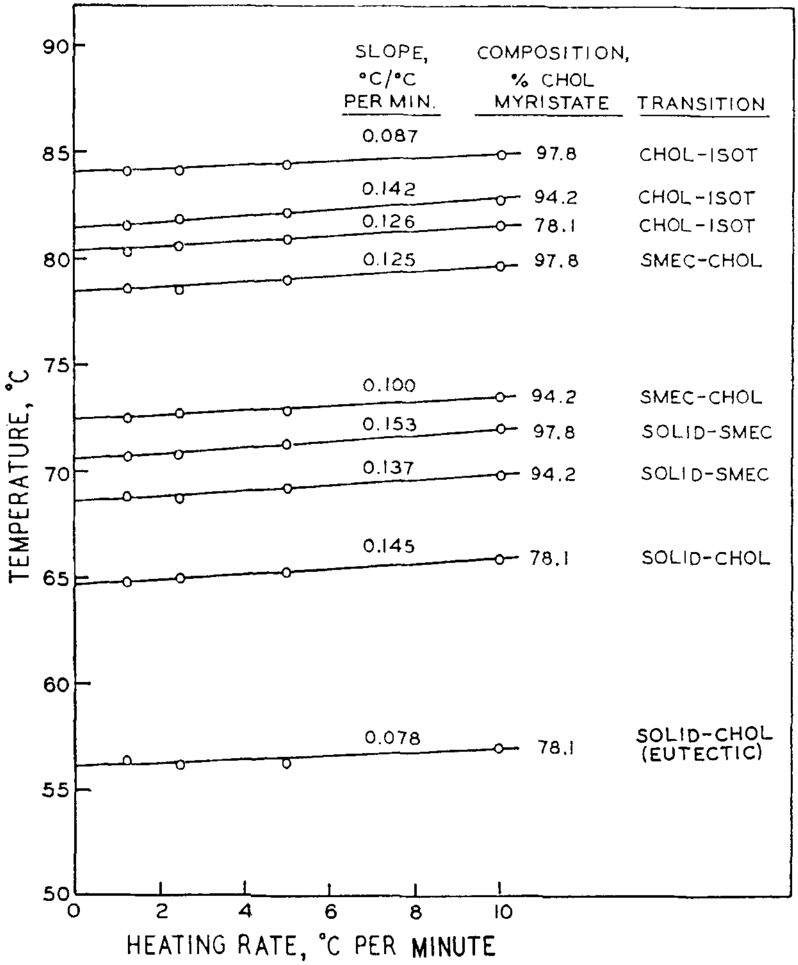

Figure 3. Transition temperatures vs. heating rate in DSC—cholesteryl myristate–cholesteryl acetate.

similarity in slope and the linearity of correlations. From these results, a correction of 1.2 °C is subtracted for a heating rate of 10 °C per minute and proportionately less for slower rates. This is clearly an instrument correction rather than sample behavior.

IV. Transition Separation

For compositions of greater than 94% myristate, the transition peaks were distinct, even for the mesophases, as has been previously observed.(3,4) However, for the blends with 78.1, 54.0 and 43.4% myristate in acetate see for example Fig. 4, the lower transition peaks were broad and overlapped. At the lower myristate concentrations, see for example 18.3% myristate in Fig. 5, the transition peaks for the eutectic mixture were distinct but the peaks for the remaining pure acetate melting were broad, making it difficult to establish unambiguous transition temperature, ranges and heats.

Microscopy

For the morphology study, the blends were placed on regular microscope slides, heated until melted, covered with standard cover

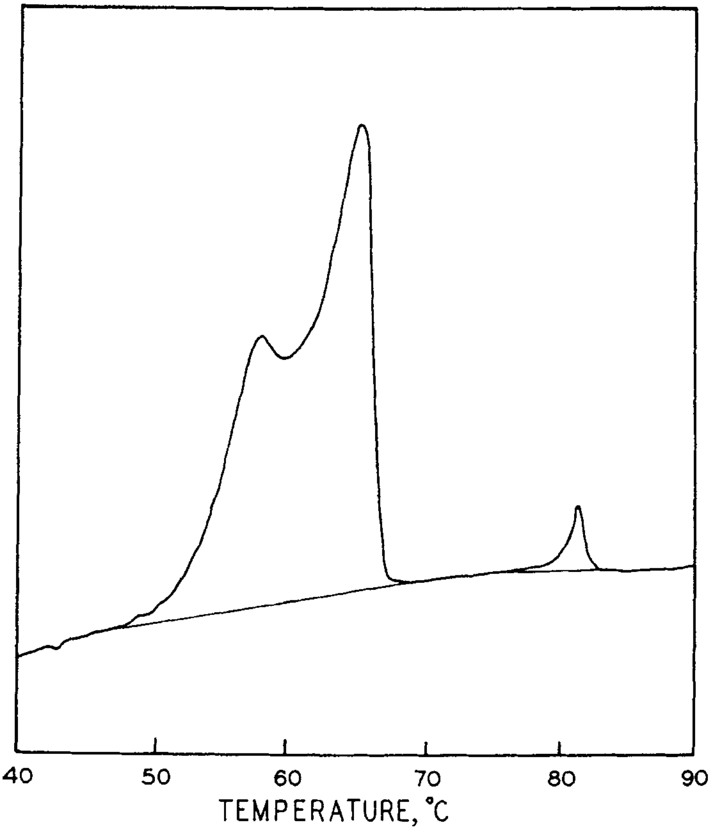

Figure 4. DSC trace—78.1% cholesteryl myristate; 21.9% cholesteryl acetate.

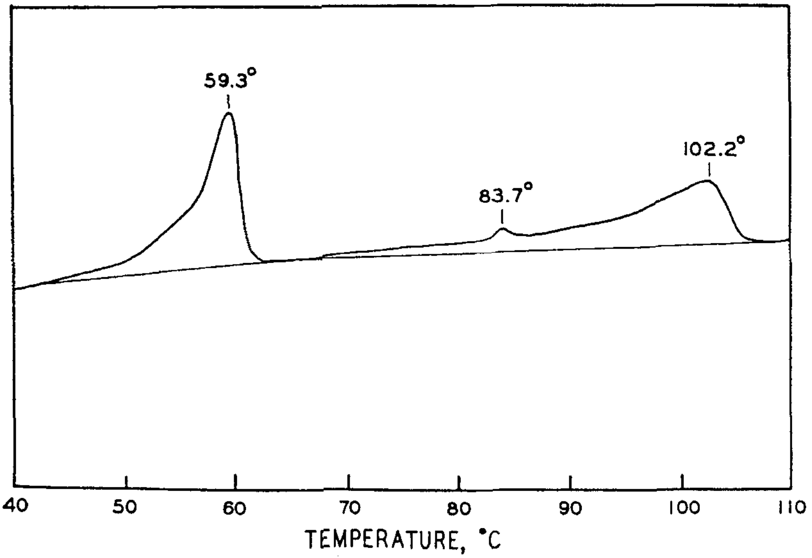

Figure 5. DSC trace—18.3% cholesteryl myristate; 81.7% cholesteryl acetate.

slides, and allowed to cool. The basic procedure for observing the textures under crossed polars of the polarizing microscope was to heat and cool the samples at 2 °C per minute on a Mettler Hot Stage. This rate is similar to the DSC heating rate of 2.5 °C per minute. Several factors not readily apparent from the thermal analysis were considered because of the different textures and broad transition ranges. Among these variables were the rates of heating and cooling, sample thickness, shear and sample history. Pictures of textures were taken with a 35 mm camera using Kodak Pan X film at one-half second exposure. The magnification after enlarging the prints was 88.2 × .

X-ray

The X-ray diffraction data were taken with an XRD–5 Diffraction Unit (General Electric Company, Schenectady, New York). The diffraction intensity was measured as a function of angle with a Geiger counter and recorded. Nickel filtered Cu K radiation was used. The sample was contained in a cell with an inner diameter of 1 cm and a thickness of 1 mm. There were two mylar windows on the cell which was attached to a heated copper block. A hole in the asbestos-insulated block permitted symmetrical transmission experiments. Sample temperatures were maintained within 0.1 °C by pumping thermostatting oil through the block. Checks were made with a thermocouple and a digital readout thermocouple. Corrections were made for scattering by the mylar windows. Results were checked for the angular position of the diffraction lines, their intensity and width.

The three blends selected for X-ray study had compositions of 31.9, 66.8, and 78.1% myristate. These were chosen to represent compositions near the eutectic point, and one on each side of the euctectic composition. From two to five temperatures were used to obtain representative structure determinations from the solid to the isotropic liquid.

3. Results

MYRISTATE–ACETATE ESTER BINARY SYSTEM

Phase Changes

Crystal–smectic and eutectic transitions. Starting with pure myristate and as the acetate content was increased, the crystal–smectic transition temperature decreased in accord with the van't Hoff equation for melting point depression due to impurity (Eq. (2). This relation held to approximately 50 mole % myristate (see Fig. 6). Similarly, starting with pure acetate, the crystal melting temperature decreased as the myristate content was increased. There was a positive deviation here from the van't Hoff equation with the resultant eutectic point observed at about 50 mole % rather than the hypothetical 63 mole % myristate from the intersection of van't Hoff lines based on known transition heats for the pure compounds. The eutectic melting temperature was constant at 57 °C throughout the range of binary compositions. The eutectic represented an additional transition which was difficult to separate from the transition for the subsequent melting of the pure component especially in compositions close to the eutectic composition, see Figs. 4 and 5.

Smectic–Cholesteric Transition. Beginning again with pure myristate and increasing the acetate concentration, the temperature for the

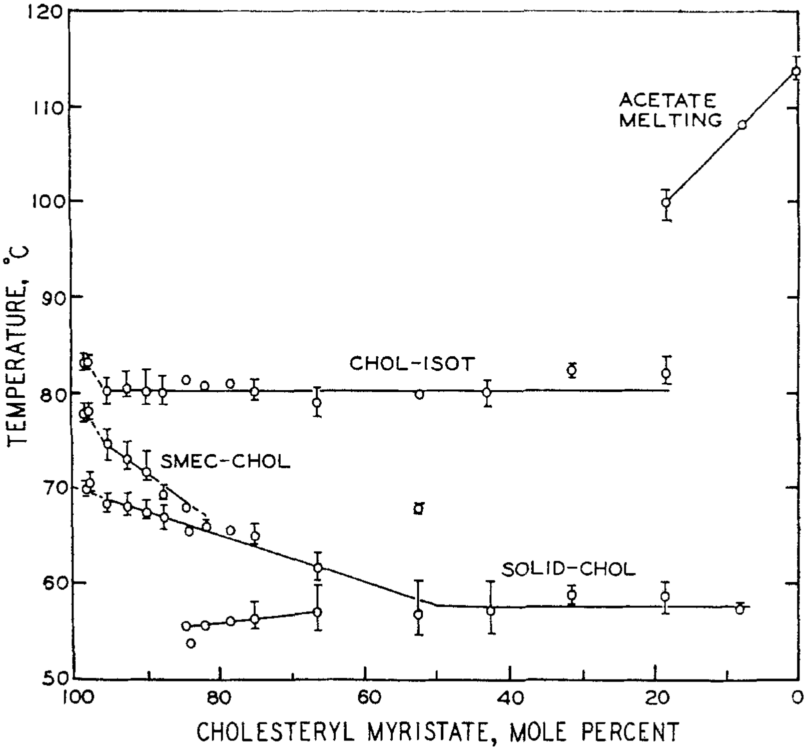

Figure 6. Phase diagram—cholesteryl myristate–cholesteryl acetate.

smectic–cholesteric transition decreased more rapidly than the decrease in temperature for the solid–smectic transition, (see Fig. 6). As a result, the smectic mesophase apparently extinguished at a composition of ~ 80% myristate where the two transition lines merge. The heat for the smectic–cholesteric transition also decreased with acetate composition and goes to zero at near the same composition as the disappearance of the smectic mesophase by the merging transition temperature lines. In cooling curves, a smectic–cholesteric transition was observed with extremely small heats down to 78% myristate and 49 °C. The smectic mesophase for myristate apparently can survive on substition of up to about one molecule in five with the acetate ester, which itself does not form a smectic mesophase.

Cholesteric–Isotropic Transition. The temperature for the cholesteric–isotropic liquid transition remained essentially constant at

80 to 82 °C for a broad range of measurable compositions. Below 40% myristate, the cholesteric–isotropic transition extended across the pure acetate melting line (see Fig. 6). In this region, the myristate and only the acetate fraction which had converted to the cholesteric comesophase transformed to the isotropic liquid. As the temperature was increased, the remaining solid pure acetate continued to convert but directly to the isotropic liquid. On cooling, the isotropic–cholesteric transition was found 94.5 °C for the purest acetate (see Fig. 6). The cholesteric–isotropic transition heats were greater for the cooling cycle when the isotropic liquid was supercooled than for the heating cycle when some of the acetate was still crystalline.

In addition, the DSC heating traces for the cholesteric–isotropic transition in many cases had a small plateau immediately preceding the regular transition peak. This has not been reported previously, probably due to the small nature of the entire transition. On cooling, the same plateau was observed on the cool side of the transition. The implication is a high specific heat or a minor transition just below the nominal cholesteric–isotropic liquid transition. This may represent the first calorimetric determination of a cholesteric textural transition. A similar effect was observed in an independent viscosity study.

Transition Heats. Transition heats for the binary acetate systems agree with conclusions concerning eutectic formation. Figure 7 displays the eutectic heats, the melting heat of the additional pure component and the total transition heats. Extrapolation of both the eutectic heats and the heats for the pure components support a eutectic composition of 50 mole %, the same as obtained from the phase diagram. The values for total heat are below the linear interpolation of total heats for the individual components. This is true even after inclusion of a small term for the entropy of mixing which is maximum at the eutectic. The deviation is also greatest at the eutectic composition where the deviation from the van't Hoff equation is greatest, indicating a maximum deviation from ideal mixing.

The transition heat for the smectic–cholesteric transition decreased with myristate content as discussed earlier. The cholesteric–isotropic

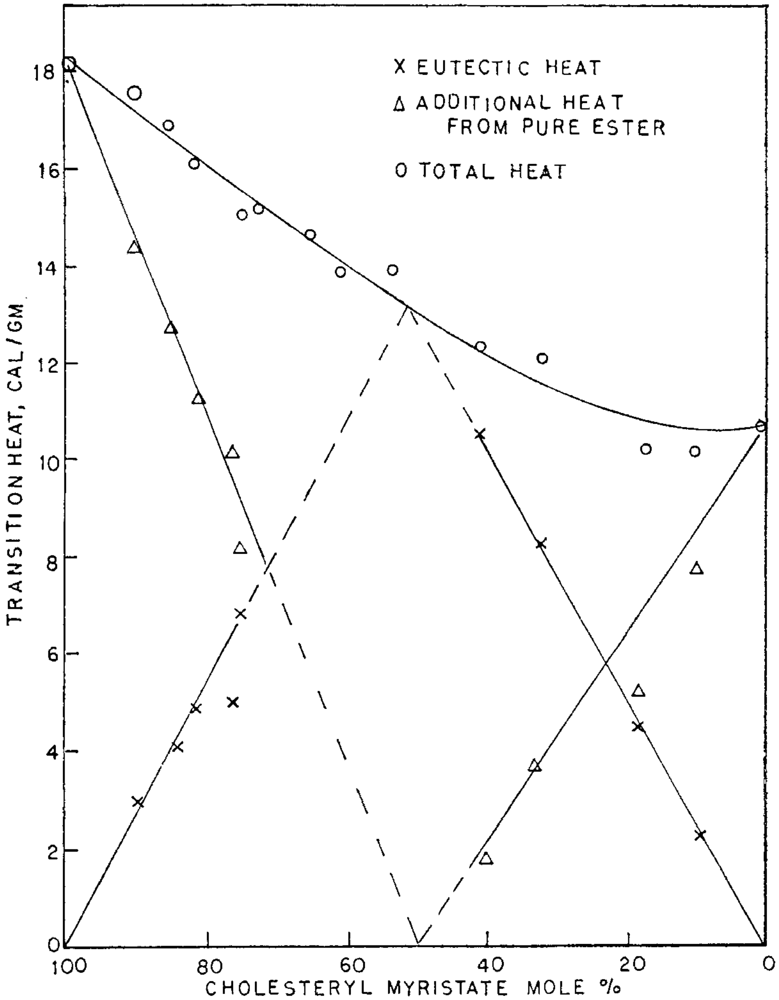

Figure 7. Crystalline melting transition heats—cholesteryl myristate–cholesteryl acetate.

transition heat is essentially independent of composition. This further supports the coexistence of both myristate and acetate in the cholesteric mesophase. At below 40% myristate, the transition heat decreased and was difficult to establish. This is consistent with the presence of the pure acetate crystal which has not melted and hence does not undergo a transition to the cholesteric mesophase on the heating cycle. A larger heat, equal to other compositions, is observed on cooling the melt as long as the solid acetate has not formed.

Microscopy. The textures within phases were not readily found by calorimetry. Numerous changes in the pure esters were, however, readily observed by light microscopy; these changes were not limited to a single specific texture for any one phase or temperature. Most of the textures could be related to specific phases or combinations of phases with a dependence on thermal history. The cholesteric–isotropic liquid transition was the most clearly observed. It was obscure, however, in the low myristate compositions where the cholesteric mesophase changed to isotropic liquid before all the pure acetate had melted. For melting of the eutectic and the subsequent gradual melting of the remaining pure component, there was a continuous morphological change from the solid to the isotropic liquid with discontinuities at the mesophase transitions.

Textures observed on the cooling cycle were more descriptive but they were seldom the same as those observed on heating. All samples on cooling were homeotropic in the cholesteric phase for several degrees below the isotropic transition, depending on time and temperature. The focal–conic texture formed as spherulites resembling, under cross polars, white poinsettas or carnations with black edges. The focal conic smectic mesophase, which was beautifully colored under polarized light, required slow cooling for formation. The stable crystalline form also exhibited spherulites on cooling from the melt. An example is given in Fig. 8. It shows under crossed-polars the cholesteric–solid transition for 46% acetate. Cooling was at 2 °C per minute with the temperature held at 30 °C for the formation of the crystalline spherulite shown in the center of the cholesteric mesophase.

The solid–smectic transitions occured rapidly on heating as did the smectic–cholesteric transitions on both heating and cooling. This is in contrast with the slower spherulitic type formation of the focal conic texture from the homeotropic cholesteric texture and the formation of the crystalline solid from the smectic or cholesteric mesophases. Of particular interest was the 78% myristate blend which exhibited a spectral absorption change on cooling in parts of the sample at 56.5 °C to 54.5 °C going from purple to red with a color

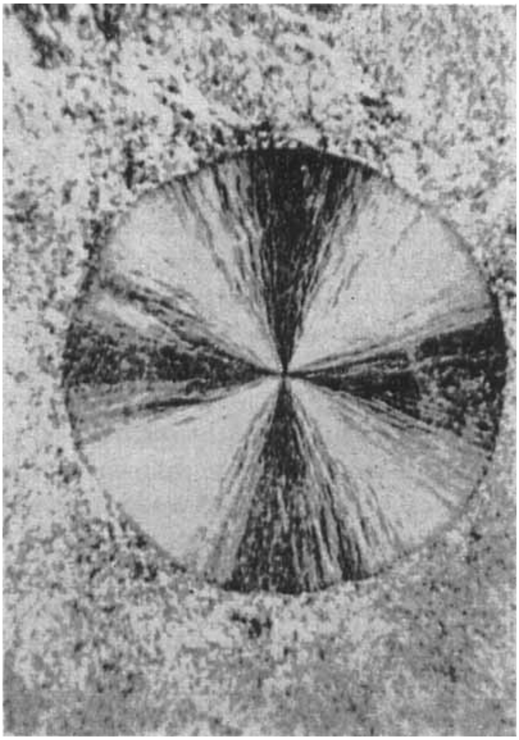

Figure 8. Cholesteric to solid transition at 30 °C for 46% acetate ester in myristate ester.

change approximately every 0.5 °C. This change with temperature was not time dependent; it could be reversed on heating or maintained at a constant color. Color changes in some of the other acetate blends were observed but were not as readily reproduced. Extensive additional microscopy was performed on these systems, and the results can be supplied on request.

X-ray Diffraction. X-ray diffraction was used primarily to identify structures in the pure and mixed crystals. This was especially useful for defining conditions where the eutectic had melted and the remaining crystals of a pure ester continued to melt over a wide temperature range. Evidence for structure changes of this nature were suggested by both DSC and microscopy. X-ray diffraction was required;

however, for specific identification. Three different blends were analyzed with the following results:

1. 78.1% cholesteryl myristate (83.5 wt %)—at room temperature, the mixture contained two independent crystals as shown by the unit cell parameters. From the intensities of the specific reflections, the weight percent myristate was calculated as 80%. At 60 °C by X-ray, all of the acetate and 32% of the myristate had melted. This placed the mixture above the eutectic temperature. It also indicated a myristate melt transition at 53% myristate at 60 °C (consistent with the 59% from the phase diagram). At 70 °C, no solid phase was present by X-ray. The small angle peak indicated a cholesteric mesophase. The *d*-spacing and high-angle diffraction indicated a mesophase mixture.

2. 66.8% cholesteryl myristate (73.7 wt %)—at room temperature, the mixture exhibited by X-ray two independent crystals with a weight percent of 78% myristate. This composition was selected as being near the eutectic. Thus at 66 °C, the sample was observed as a mixture of myristate and acetate in a cholesteric comesophase.

3. 31.9% cholesteryl myristate (39.5 wt %)—at room temperature, the mixture exhibited the two independent crystal structures of 38 wt % myristate. At 66 °C, the myristate had all melted and 44.6% of the acetate was melted; at 77 °C, 67.5% of the acetate was melted. The results indicate that the mobile phase is cholesteric on comparison with results for the pure esters. At 87 °C, 86.6% of the acetate had melted and a broad, low-angle reflection indicated an isotropic liquid. At 95 °C, there was only a broad peak identified by X-ray *d*-spacing as an isotropic liquid mixture.

From the amount of acetate melted, compositions of liquid in equilibrium with acetate crystals were calculated to determine the deviation from the van't Hoff equation. By X-ray the liquid was 35, 41 and 52% myristate at 87, 77, 60 °C, respectively. X-ray results thus support the location of the eutectic composition at 50% and 57 °C as determined from the transition temperatures and heats.

CHOLESTERYL MYRISTATE–CHOLESTERYL NONANOATE BINARY SYSTEM

From the extensive results on the cholesteryl myristate–acetate system, a model phase diagram can be proposed for other binary systems. This is established by assuming a simple eutectic system of mixed crystals and with complete ester miscibility in the mesophases and in the isotropic liquid. The cholesteric–isotropic liquid transition and the smectic–cholesteric transition are assumed to exhibit a linear relation between transition temperatures for pure esters, following Raoult's law. The eutectic point is established by calculating the crystalline melting point depressions due to impurity (using van't Hoff equation and literature values for transition heats and temperatures), for both of the pure components and using the point of intersection as the eutectic temperature and composition. A horizontal line is generated at the eutectic composition to express the eutectic melting temperature. These concepts were tested with a second binary system, cholesteryl myristate plus nonanoate. The transition temperatures and heats for the pure components and a series of blends were determined by DSC. The results are shown in

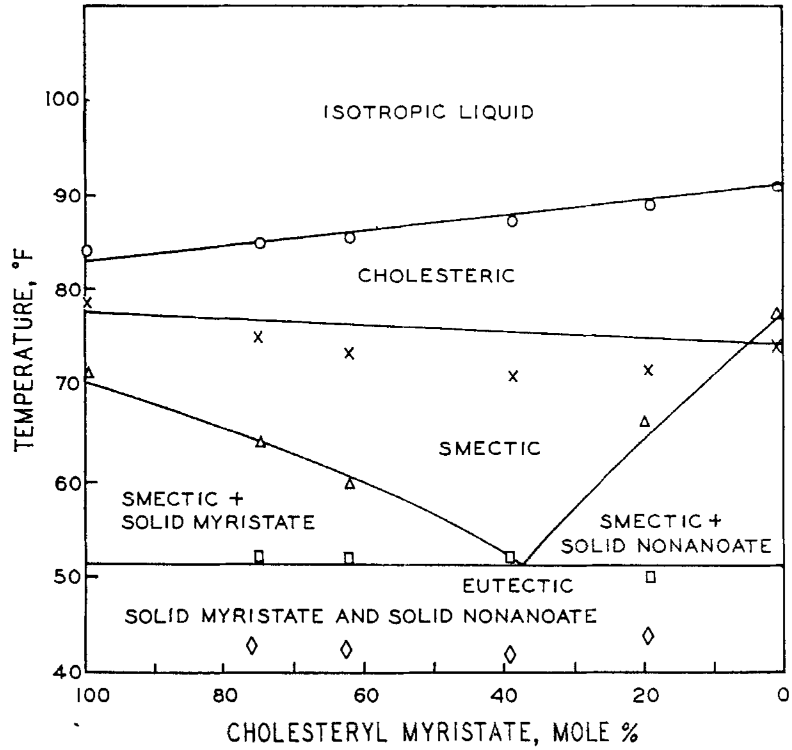

Figure 9. Phase diagram—cholesteryl myristate–cholesteryl nonanoate.

Fig. 9. The cholesteric–isotropic liquid transition temperatures are in excellent agreement with prediction. There is only a minor depression near the center, indicative of nonideality. The nonanoate and myristate esters thus indeed do form a single cholesteric comesophase and similarly a single isotropic liquid. They also form a single smectic comesophase again with minor nonideality (see Fig. 9). The melting

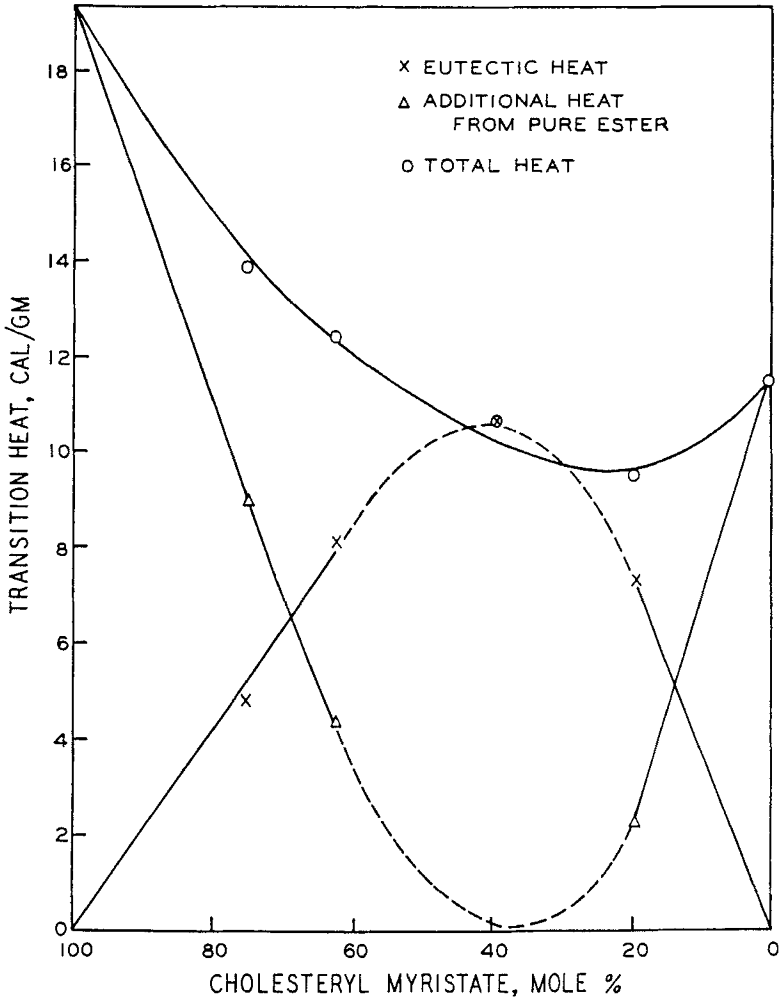

Figure 10. Crystalline melting transition heats—cholesteryl myristate–cholesteryl nonanoate.

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temperatures for both the eutectic and the excess pure components agree well with the values calculated from the proposed model.

At 43 °C, an endotherm was observed for all nonanoate blends. At 75% myristate, this transition was just evident. As the nonanoate composition was increased, the transition heat increased to the extent, that for the 20% myristate blend, the curve was not readily distinguished from the eutectic transition at 52 °C. No such transition was observed for the pure nonanoate. The effect is considered to be a solid–solid transition of the nonanoate induced by impurity.

Measured transition heats for the eutectic agree well with values calculated on the simple addition of heats for the individual components (see Fig. 10). Also, extrapolation of the heats for the eutectic and the incremental, remaining pure ester agree with the eutectic composition determined by transition temperatures. The incremental heats for the pure components when added to the eutectic heat plus the heat of mixing, however, do not agree with the theoretical total heats, indicating a deviation from ideal mixing.

4. Conclusions

The binary systems of cholesteryl esters form eutectics at the crystalline transition. The solid melting transitions for each component follows the van't Hoff equation (for melting point depression due to impurity) exactly at low dilution. The intersection of van't Hoff lines approximates the measured eutectic temperature and composition. This means that the esters are separated only at the lowest transition temperatures. The van't Hoff equation of course does not apply to the cholesteric transitions—since they do not involve compositional variations. The mesophases thus form homogeneous mixtures with transition lines connecting the mesophase transitions of the pure components. To be sure such lines must, in theory, represent flat loops. This is difficult to estimate from broadened peaks for blends and the deviations from Raoult's law are also minor for the cholesteric transitions of blends. The transitions for the blends were not generally, however, as sharp and distinct as for the pure components. The blends exhibit single smectic and cholesteric mesophases.

The general criteris developed here may be used for other ester blends to aid (a) in selection of compositions to be tested, (b) in determination of conditions and methods of testing, and (c) in defining ternary and higher order systems. This is especially important in systems having multiple mesophase regions and broad transition temperatures. Deviations from the proposed model phase diagrams are readily detected. Among complexities are (a) monotropic mesophases, (b) relatively low transition heats which are even more difficult to determine in blends, (c) solid–solid transitions, and (d) relatively high transition heats for the solids which result in low slopes for the solid melting line in the phase diagrams.

To minimize the temperature range for the cholesteric mesophase, an ester, say myristate, may be combined with another ester with a narrow cholesteric transition range and similar structure, such as with cholesteryl pentadecanoate, to form a nearly ideal mixture. This might limit the cholesteric mesophases to temperatures of 78–83 °C for all binary compositions. Conversely, to increase the cholesteric temperature range, the myristate might be combined with another ester which also forms a cholesteric phase but with a much higher or lower isotropic transition temperature. Although the cholesteric mesophase range was extended by blending with the acetate ester, the effective thermographic color range extended only over 2 °C just prior to the cholesteric–smectic transition.

Blends may be used to evaluate mesophase transitions by depressing the melting temperature of the solids. This may be significant in studying the smectic mesophase in esters such as octanoate, heptanoate, and hexanoate and other esters exhibiting monotropic transitions. The possibility of smectic mesophases in esters of less than eight carbons might also be investigated.

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