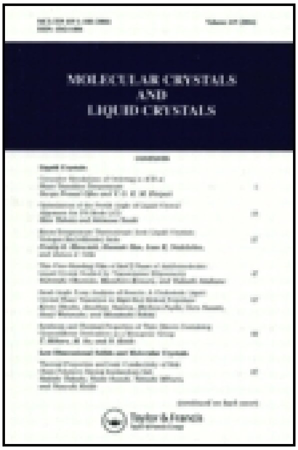

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The Viscosity of Mesophases Formed by Cholesteryl Myristate

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Abstract—This investigation provides the first reported viscosity measurements on cholesteryl myristate. Viscosities were measured as a function of both temperature and shear over temperatures corresponding to the isotropic liquid, the cholesteric mesophase, and the smectic mesophase. The myristate ester was chosen for study because its multiple phase transitions have been previously shown to be reproducible. The phases also persist over relatively long temperature ranges. The viscosity measurements were made at lower shear rates than previously reported for esters of cholesterol by using a Weissenberg Rheogoniometer. These are the first cone-and-plate viscosity measurements reported for any esters of cholesterol. The shear rates in this cone-and-plate viscometer are homogeneous and variable. The results show large breaks in viscosity behavior at the independently-measured thermodynamic transitions between the crystal, smectic, cholesteric, and isotropic states. Viscosities for the isotropic state are Newtonian throughout. The viscosities for both the cholesteric and smectic mesophases are prominently non-Newtonian with a sharp transition between the two. This is the first time a change in rheology has been reported at a smectic-cholesteric transition. A prominent viscosity maximum is observed near the cholesteric-isotropic transition which depends on shear rate and perhaps on time of shearing.

‡ On leave from Mitsubishi Chemical Industries Limited, Tokyo, Japan.

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Part 15 of a series on Order and Flow of Liquid Crystals.

Introduction

A classification method for mesophases was introduced by Friedel in 1922.[1] Friedel distinguished two types of mesophases on the basis of internal structure, the nematic and smectic forms. These two basic types correspond to a classification made by Lehmann on the basis of mesophase viscosity.[2] The nematic type was called liquid crystalline because of its low viscosity, about 1 centipoise. Smectic mesophases were called flowing crystals, corresponding to viscosities reportedly about 10 times higher.[2] Certainly more information is needed since nothing like a complete rheological theory nor even a general method of viscosity classification has been offered for mesophases.[3]

It has been a goal in the studies of these workers for some years to develop more definitive and general rheological classifications for mesophases. A basic limitation to date has been the lack of definitive data on the flow characteristics of the third basic type of mesophase, the cholesteric mesophase. To be sure, several studies have been published on the flow of esters of cholesterol which can exhibit a cholesteric mesophase. Prior viscosity studies have included the acetate,[4-6] propionate,[4,5,7] butyrate,[4,5] hexanoate[8], nonanoate,[8] palmitate,[4] stearate,[4] benzoate,[9-13] and ethyl carbonate[5,6,14] esters of cholesterol. Many of these compounds, however, also exhibit a smectic mesophase as well as a cholesteric mesophase. Moreover, the previous studies of these workers do not show any discontinuity in viscous behavior at temperatures expected for the smectic-cholesteric transitions in the ester series. An added complication is that the temperature range for the cholesteric mesophase in some of the esters studied, e.g. palmitate and stearate, is very small, about 2 °C. It has therefore been uncertain as to whether the viscosities reported in the mesophase range for the higher esters of cholesterol correspond to those for the smectic and/or for the cholesteric mesophase. The purpose of this study is to evaluate the flow characteristics in a different configuration, and under different shear conditions using an ester of cholesterol for which the phase transitions are well established

This procedure was chosen to single out the characteristic flow properties of the cholesteric type of mesophase.

The non-Newtonian quality of mesophases formed by esters of cholesterol was first pointed out by Ostwald in 1933.[5,6] He reported viscosity measurements as a function of temperature and shear for the isotropic and mesophase ranges for cholesteryl acetate, propionate, and butyrate. The present workers subsequently reported studies on cholesteryl palmitate and stearate as well as a reinvestigation of the acetate ester.[4] Recently, all the rheological data available on mesomorphic states have been evaluated in a review.[3] In general, it can be said that the rheological properties of mesophases formed by esters of cholesterol are still far from understood.

This paper provides the first flow data available on an intermediate aliphatic ester of cholesterol, the myristate ester. This compound was chosen for detailed studies for several salient reasons. The transition temperatures and heats of transition for the myristate ester are the most well established among all esters of cholesterol.[15,16] The transition temperatures and heats have also been shown to be independent of sample history, i.e. independent of the solvent chosen for recrystallization and independent of the cooling rate for crystallization from the melt. Reproducible crystallization features are not found in many of the other esters previously investigated in rheological studies.[4–6,16,17] Table 1 provides transition temperatures for cholesteryl myristate as reported in the literature and as obtained on the sample used in these studies.[15–18] Transition temperatures

TABLE 1 Transition Temperatures for Cholesteryl Myristate

	Mesophase Transition Temperatures		
Information Source	Crystal-Smectic	Smectic-Cholesteric	Cholesteric-Isotropic
Literature	73.6	79.9	85.5
This Work by DSC	70.8	77.8	82.9

obtained here by calorimetric means are also subsequently compared with those determined rheologically. An excellent correspondence, within 1°, is observed. Indeed viscosity measurements have provided a sensitive measure for phase transitions including, for the first time, a distinction between a cholesteric and a smectic mesophase.

The measurement technique used in this study involved exclusively the Weissenberg Rheogoniometer. This instrument provides viscosity measurements as a function of shear rate and temperature over a considerable range of these variables. In previous studies on cholesteryl esters, Schenck used capillaries to study the flow of the benzoate ester.[11] Ostwald also used capillaries to study the flow of the acetate, propionate, and butyrate esters,[5,6] whereas Porter and Johnson used capillaries as well as a concentric cylinder viscometer to study the rheology of the acetate, palmitate, and stearate esters.[4] This investigation reports the first mesophase rheology obtained in a cone-and-plate geometry.

Experimental

MATERIAL

The cholesteryl myristate used for study was obtained from the Eastman Organic Chemicals Company, Rochester, New York. Table 1 compares the highest transition temperatures reported in the literature for this compound with those measured by DSC at atmospheric pressure on the rheological samples. The multiple transitions were measured here by using a differential scanning calorimeter, a Perkin-Elmer DSC-1B. The observed transition temperatures are slightly lower, about 2 °C, than the highest values in the literature. The difference is likely due to a small purity difference between the sample studied here and the most pure samples of the ester previously isolated. These tests required large amounts of material and sample purification was not undertaken: it should therefore be kept in mind that effects of impurities may be operative.

MEASUREMENTS

All viscosities were measured by means of a cone-plate type instrument, the Weissenberg Rheogoniometer, Sangamo Controls Company. Most measurements were made in order of decreasing temperature while holding the shear rate constant at a series of different values. This technique involves calibration of gap setting between the cone-and-plate as a function of temperature. This calibration provides a method for making instrument adjustments in order to hold the gap width constant during continuous shear measurements as a function of temperature. Additional measurements were made as a function of shear rate at a series of constant temperatures. Agreement of results from the two types of measurements was reasonably good, better than 5%. On the log scales used in the figures, the difference between measurements is negligible.

Results and Discussion

Figure 1 shows viscosity results on cholesteryl myristate as a function of shear rate. Measurements are given at a series of constant temperatures which cover the smectic, cholesteric, and isotropic liquid phases for the ester. Figure 2 shows viscosity data as a function of temperature. This is a cross-plot of the data in Fig. 1 with incorporation of additional and different data. The rotational cone-and-plate viscometer used in these studies not only provides a homogeneous shear rate but a method for measuring viscosity at specific shear rates as a continuous function of temperature. Thus tests were made on cholesteryl myristate while transcending the temperatures for the characteristic transitions described in Table 1. All the thermodynamic transitions are readily observed rheologically and the characteristic flow behavior is detailed for each state. The rheologically-observed transitions agree closely with those measured independently by differential scanning calorimetry. This means that orientation forces in shear do not appreciably alter the order change at the phase transitions. Figure 2 indicates rheological transitions at 83 °C, 77–78 °C, and a variable transition for crystal formation within a few °C of the thermodynamically measured phase transformation.

Table 2 provides flow activation energies for the smectic and isotropic states of cholesteryl myristate. The activation energy, E^*, is derived from the change of absolute viscosity, η, with

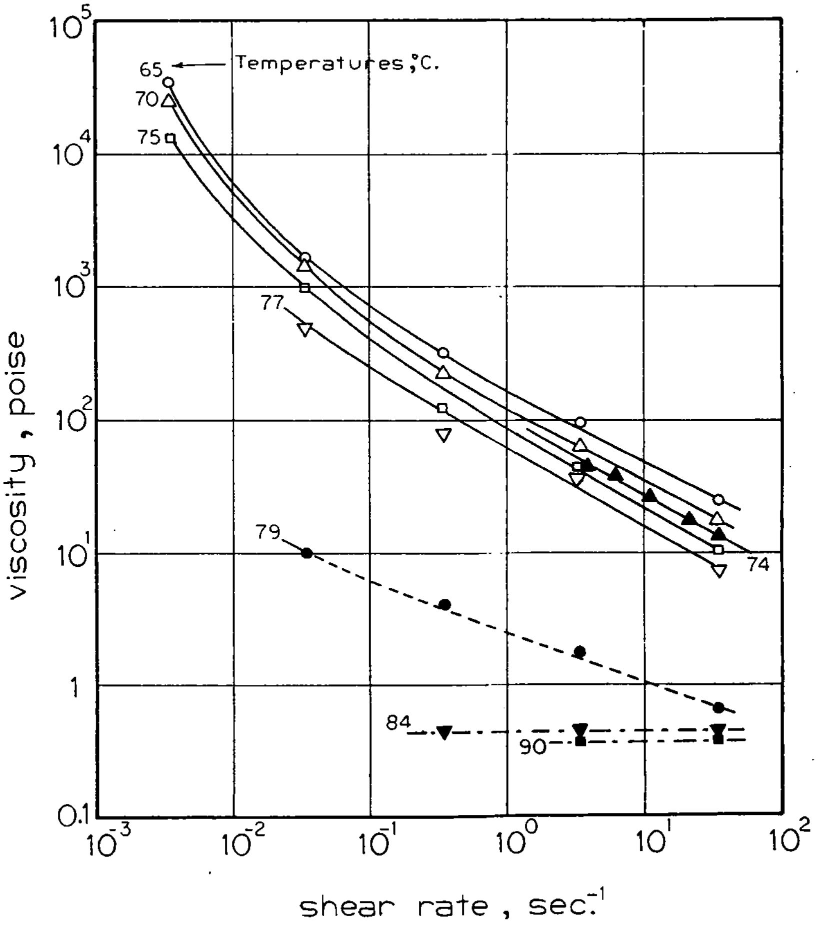

Figure 1. Cholesteryl myristate: viscosity change with shear rate.

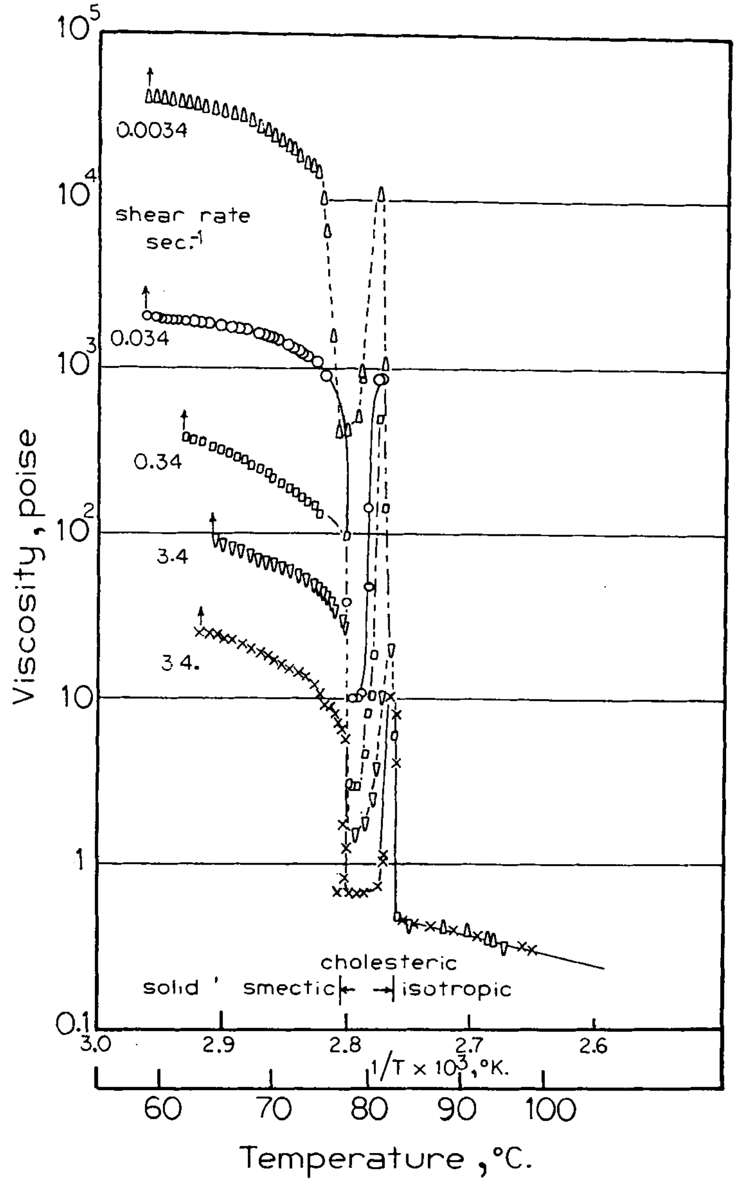

Figure 2. Cholesteryl myristate: viscosity change with temperature.

absolute temperature, T.

$$\ln \eta = E^*/RT + A$$

where R is the gas constant and A is a constant. The activation energies for the myristate ester are compared with corresponding values available for other esters of cholesterol. The activation energies and viscosities are similar for members of the ester series investigated to date. Indeed, the viscosities for the higher and lower molecular weight esters have been shown to be close to 22 centipoise at 117 °C[4], in agreement with an extrapolation of data in Fig. 2. Both kinematic and absolute viscosities for the isotropic states appear to be equivalent within precision of present measurements for the series above acetate through stearate. Importantly, all the esters are found to be Newtonian in the isotropic state over the measured shear rate ranges of from 10^{-1} to 3×10^5 seconds^{-1}. The lower shear rates were measured in this study using the cone-and-plate viscometer whereas measurements on other esters at higher shear rates were made with a concentric cylinder viscometer.[4]

TABLE 2 Flow Activation Energies for Esters of Cholesterol

	Flow Activation Energies, Kcal/mole	
Ester	Liquid Crystal	Isotropic Liquid
Acetate	15.5	11.9 (125 °C)
Myristate	11 to 16	8.2 (100 °C)
Palmitate	10	8.1 (125 °C)
Stearate	11.9	8.0 (125 °C)

The sharp viscosity changes observed at the smectic-cholesteric and cholesteric-isotropic transitions, see Fig. 2, correspond to unusually small first-order transitions of 0.5 and 0.4 calories/gram, or only about 2% of normal fusion heats.[16] In general, liquid crystals, including the myristate ester, are more liquid than crystal, with far the largest transition heat exhibited at the lowest temperature transition, i.e. for the crystal-mesophase transformation.[16]

A remarkably steep viscosity maximum on the temperature axis is observed near the cholesteric-isotropic transition, see Fig. 2. This maximum was found to be quite unstable. When this state was kept at constant temperature, ± 0.1 °C for a few minutes under continuous shear, the viscosity was found to decrease with time. The changes are within a relatively large envelope on the temperature scale near the transition. It has been widely supposed that this type viscosity maximum is just as characteristic of the cholesteric as it is for the nematic mesophase.[18] This is not true, as has been pointed out by Lawrence.[7] The peak maximum for the cholesteric mesophase not only varies with time at constant shear rate and temperature, but decreases markedly with increasing shear rate, and, indeed, completely disappears in tests at the highest shear rates. This result has been documented and republished[7,18,19] for several other esters of cholesterol,[5-7] the ethyl carbonate, the propionate, the butyrate, notably the acetate,[4-7] and is confirmed here with data on the myristate ester. The shear rates and stresses used here are lower than in earlier tests on other esters, yet the peak maximum near the cholesteric-isotropic transition has virtually disappeared at relatively low rates of shear, see Fig. 2.

The viscosity peak for esters of cholesterol near the isotropic transition is reportedly symmetrical. This is essentially the case for the myristate ester. These studies of the viscosity maximum are the first to be made in continuous shear while crossing the transition temperature. All previous reports of the maximum have been made in capillaries with the inherent limitation of measurements at discrete temperatures and at non-homogenous shear rates. It has been the conclusion of Lawrence, which is consistent with the present results, that the viscosity maximum near the transition is due to some type of turbulent effect.[7] The height of the maximum could be therefore a qualitative measure of the amount of cholesteric mesophase transformed to the isotropic liquid.

True viscosities for the cholesteric mesophase, free of the peak near the isotropic transition, appear to change markedly with rate of shear, see data at 79 °C in Fig. 1. The true flow characteristics of the cholesteric mesophase likely correspond closely to values near the minimum between the viscosity increase at lower temperatures in the smectic mesophase and the increase near the cholesteric-isotropic transition. Viscosities near the minimum decrease regularly and sensitively with rate of shear. Importantly, the minimum for the case of highest shear rate, 34 seconds^{-1}, is located near the extension of the viscosity line for the isotropic phase, see Fig. 2. It may therefore be postulated that (1) a minimum viscosity for the cholesteric mesophase has been reached at only moderate shear rates, (2) that the viscosity peak near the isotropic transition likely disappears at high shear rates, and (3) the high shear limiting viscosities for the cholesteric mesophase can be closely predicted by an extrapolation to lower temperature of viscosities for the isotropic liquid, see Fig. 2. This same limit likely holds for the smectic phase, but higher shear rates are required. The results of this study also indicate that viscosities for the cholesteric mesophase are relatively low compared to the smectic mesophase. The viscosities for both mesophases are markedly shear dependent, see Fig. 1. Quite another behavior is observed for the nematic type of liquid crystal. Viscosity tests thus represent a simple, sensitive, and definitive method for distinguishing smectic and cholesteric mesophases from those of the nematic type.

Limiting high shear viscosities for cholesteric and smectic mesophases can be reached. This occurs at shear stresses of about 10^5 dynes/cm^2 for systems studied to date. The cholesteric mesophase studied here has reached a high shear limit at two decades lower than the smectic or at about 10^3 dynes/cm^2.

The limiting high shear viscosities for the mesomorphic states do not necessarily imply the complete shear destruction of mesophase structures. In fact the viscosity peak near the cholesteric-isotropic transition can only come from changes involving mesophase structures. The non-Newtonian flow of the cholesteric and smectic mesophases must be due in part to orientation of the structures. This conclusion comes from previously published photomicrographs of these workers for cholesteryl myristate in the sheared as well as the unsheared state.[3] The smectic mesophase is observed to disintegrate under shear to give a spherulitic structure. The cholesteric mesophase reforms into a weak netlike structure that is oriented in the direction of shear. Such structures are broken under shear stress with the associated viscosity decrease with increasing shear rate.

Rheological documentation of mesophase-mesophase transitions of any type are relatively rare.[3] These results on cholesteryl myristate show for the first time a distinct viscosity anomaly at a smectic-cholesteric transition. A relatively sharp viscosity transition is observed at the smectic-cholesteric transition at low rates of shear. It should be emphasized, as is clearly indicated in Fig. 2, that the magnitude of viscosities and the viscosity changes at mesophase-mesophase transition are markedly dependent on shear, with both the absolute and changes in viscosity becoming less at higher rates of shear.

In earlier studies on other esters of cholesterol, no break was observed in viscosity data on transcending the temperature region for smectic-cholesteric transitions.[4] It should be pointed out, however, that the studies on the palmitate and stearate esters were performed at much higher rates of shear, $> 2 \times 10^3$ seconds^{-1}.[4] This is about two decades higher in shear rate than examined here, see Fig. 1. Indeed an evaluation of Figs. 1 and 2 indicates that at higher shear rates (a) viscosities of both mesophases, smectic and cholesteric, may fall on a linear extension of viscosities for the isotropic state, and that (b) viscosities over the temperature range for the smectic and cholesteric mesophases may become indistinguishable.

Unlike the high shear limit, low shear limiting viscosities have not been measurable on smectic and cholesteric mesophases. This is because low shear viscosities are too high and may actually exhibit a yield stress. The mesophase viscosities are hypersensitive to shear with values changing a 1000 fold for only a slightly larger range of shear rates.

Table 2 gives the flow activation energy for the smectic mesophase. The values for the myristate ester are notably independent of shear rate even as viscosities change markedly with shear rate, see Figs. 1 and 2. This is consistent with the fact that the activation energies for other esters are of comparable value, see Table 2. It should also be noted that the plots of log viscosity versus $1/Tc_K$ are not entirely linear, meaning a change of flow activation energy with temperature. The results given here for the myristate ester differ from those reported earlier for the acetate, palmitate, and stearate in the sense that the curvature, and thus the change in activation energy with temperature, for the smectic mesophase are in the opposite direction.[4] Activation energies for the smectic mesophase are not influenced by either sample purity or shear rate. In contrast, absolute viscosities are markedly lower for tests on lower purity samples.[4-6]

Viscosity measurements at constant shear rate on cholesteryl myristate were generally made in the order of decreasing temperature. As the temperature approached the crystal-smectic transition. viscosity increased abruptly beyond the point of measurement. The abrupt increase apparently corresponds to stable crystal formation. The temperature for this rheological transition did not exhibit a regular trend with rate of shear, see Fig. 2. The rheological transition in general is lower than the corresponding values by DSC. This may be due to supercooling. A shear reduction of the equilibrium transition temperature is also a possibility.

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