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The Viscosity of Mesophase Blends: The Cholesteryl Acetate-Myristate Pair

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This report presents viscosity measurements on blends of cholesteryl acetate and myristate. Viscosities were measured as a function of composition, shear and temperatures over ranges corresponding to the isotropic liquid, and the cholesteric and smectic mesophases. The myristate ester was chosen as the principal constituent because its multiple phase transitions have been previously shown to be reproducible. The acetate was chosen for the blends because several workers have presented viscosity data on the neat ester. The measurements were made using a Weissenberg Rheogoniometer. 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 phase are Newtonian throughout. The viscosities for both the cholesteric and smectic mesophases are prominently non-Newtonian with a sharp transition between the two. A pronounced viscosity maximum is observed near the cholesteric-isotropic transition which depends on shear rate, time of shearing, and temperature programming derection. Results give sensitive transition data from which a phase diagram – including textures – may be defined since transformations are in agreement with thermal analyses indicating no measurable variation of transitions with shear and intensity.

INTRODUCTION

A classification of mesophases was suggested by Friedel in 1922[1]. Two of the basic types correspond to a classification made by Lehmann on the basis of

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mesophase viscosity[2]. The nematic type was called liquid crystalline because of its low viscosity, a few centipoises. Smectic mesophases were called flowing crystals, corresponding to viscosities reportedly about 10 times higher[2]. Certainly more than qualitative information is needed, however, since nothing like a complete rheological theory nor even a general method of viscosity classification has been offered for mesophases[3,4]..

A basic limitation has been the absence of data on mesophase blends. Yet several studies have been published on the flow of the individual cholesteryl esters. Prior studies have involved the formate[5], acetate[5-8], propionate[7-9], butyrate[7,8], hexanoate[10], nonanoate[10], myristate[11], palmitate[5,6], stearate[5,6], benzoate[5,12-16], and oleyl[17] and ethyl carbonate[7,8,18] esters of cholesterol. Many of these compounds exhibit a smectic as well as cholesteric mesophase. Previous studies on neat esters, exclusive of the myristate[11], do not show a viscosity discontinuity at temperatures expected for the smectic-cholesteric transition. An added complication is that the temperature range for the cholesteric mesophase in some of the esters, e.g., palmitate and stearate, is small, about 2 °C. It has therefore been uncertain as to whether the viscosities reported in the mesophase range for the higher esters correspond to those for the smectic and/or for the cholesteric mesophase.

The non-Newtonian character of mesophases formed by esters of cholesterol was first pointed out by Ostwald in 1933[7,8]. The present workers subsequently reported on cholesteryl acetate, myristate, palmitate and stearate [6,11]. The portion of these data obtained in capillaries has been given an interesting theoretical interpretation[19].

The rheological properties of blends are crucial in several ways. First, cholesterol is obtained from natural materials so that it is found with closely related compounds which can affect properties. Such ester blends are also found in atherosclerotic deposits. Ester blends are also purposely used by design in thermography because of light reflection characteristics[20]. They are also used in gas detection[21]. Ester blends are thus currently under intensive study[22-24].

The myristate ester was chosen for several salient reasons. The transition heats and temperatures for the myristate ester are the most well established among all esters of cholesterol[25,26]. 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.

This particular pair is of rheological interest because the phase diagram has been recently developed from thermal analysis along with complementary tests on the blends by X-ray and light microscopy[27]. The viscosities of acetate esters of different purity have also been published which aids interpretation[4]. The rheological tests, however, have been concentrated on compositions of high myristate content. Thermodynamic equilibrium is achievable on this side of the phase diagram. In contrast, the behavior of high acetate compositions is dominated by monotropism with the pure acetate ester having a crystal melting temperature of 116.5 °C[4]. These reversible transitions of the pure myristate ester are given in Table I.

TABLE I

Transition temperatures for cholesteryl acetate and 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	77.9	82.9
By viscosity[11]	Supercools	78.0	83.0

The transition temperatures reported in Table I are internally consistent as developed by different workers and techniques[11,25-28]. The phase diagram for this binary system is shown in Figure 1.

The viscosity technique – used exclusively – was a Weissenberg Rheogoniometer, Model R-17. This instrument provides viscosity measurements as a function of shear rate and temperature over a wide range of these variables as demonstrated with the myristate ester[11]. In previous studies on cholesteryl esters, Schenck used capillaries to study the benzoate ester[13], Ostwald also used capillaries to study the acetate, propionate, and butyrate esters[7,8], whereas Porter and Johnson have previously used capillaries as well as a high-shear concentric cylinder viscometer to study the acetate, and stearate esters[4,6].

EXPERIMENTAL

Material

The esters were obtained from the Eastman Organic Chemicals Company, Rochester, New York. Table I compares transition temperatures reported in the literature with those measured by differential scanning calorimetry, Perkin-Elmer DSC-1B at atmospheric pressure, and by viscometry[11]. The observed transition temperatures are slightly lower, about 2 °C, than the highest myristate literature values. The difference is likely due to a small purity difference between the sample studied here and the most pure esters previously isolated. These tests required large amounts of material and sample purification was not undertaken: effects of impurities may be minimal since results are presented principally on blends. The methods for blending the samples has been previously described[27].

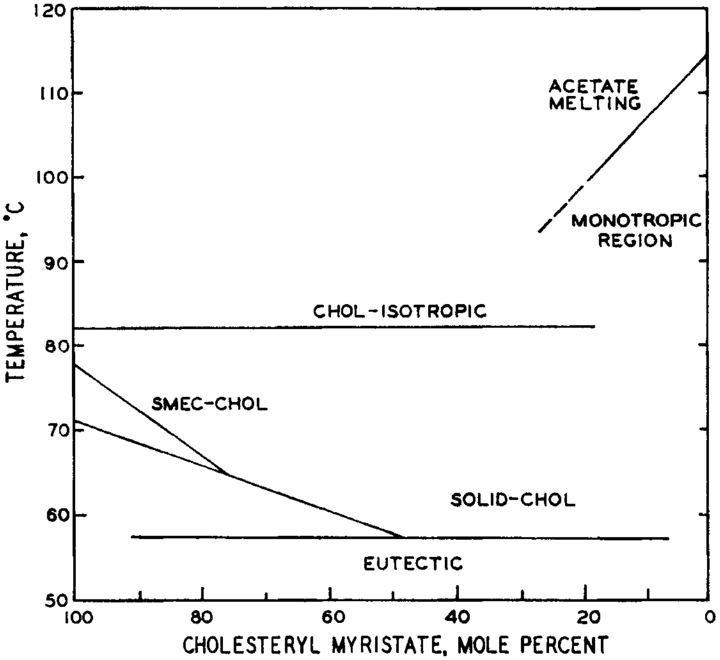
MEASUREMENTS

All viscosities were measured by means of a cone-and-plate instrument, the Weissenberg Rheogoniometer, Model R-17, (Sangamo Controls Company, Sussex, England). The steady shear measurements were made in order of continuously decreasing temperature while holding the shear rate constant. Three different shear rates (0.034, 3.4 and 34 seconds^{-1}) were used on each sample. Instrument adjustments of 1.6 microns per °C were made in order to hold the gap width between the cone-and-plate at the apex at a constant 178 microns independent of temperature. The cone angle was 4°; the radius 1.25 centimeters. The torsion spring constant, k_T, as calibrated, was 23.90. The values of t in seconds per revolution were 2.64, 26.4, and 2640 for shear rates of 34, 3.4, and 0.034 seconds^{-1}, respectively.

FIGURE I

PHASE DIAGRAM

CHOLESTERYL MYRISTATE-CHOLESTERYL ACETATE



The viscosities were calculated using the following relationship:

$$\eta = \tau/\dot{\gamma} = (3\,\Delta T\,k_T/2\pi r^3)/(360/\alpha t)$$

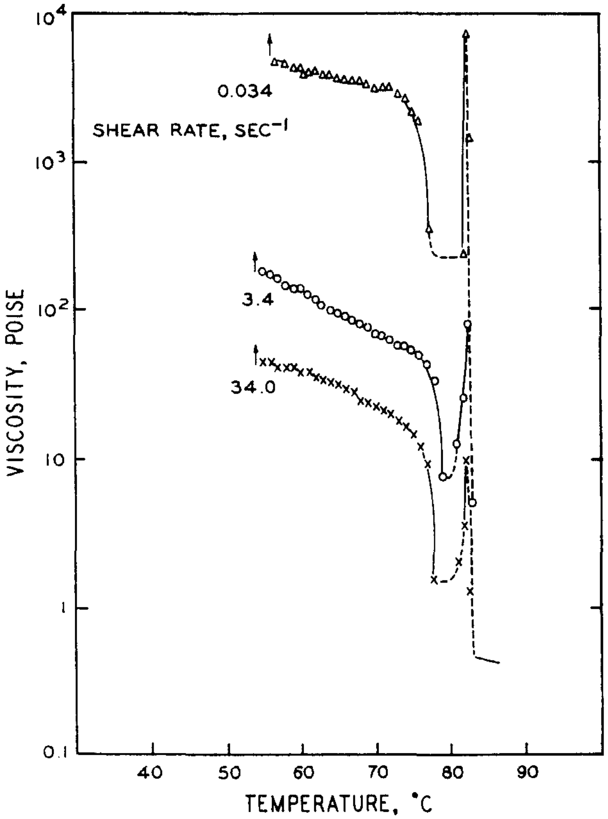
where η is the viscosity in poise (dynes-sec-cm^{-2}), τ is the shear stress, $\dot{\gamma}$ the shear rate, ΔT the movement of the torsion head transducer in microns, r is cone radius, and α the cone angle.

RESULTS AND DISCUSSION

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

FIGURE 2

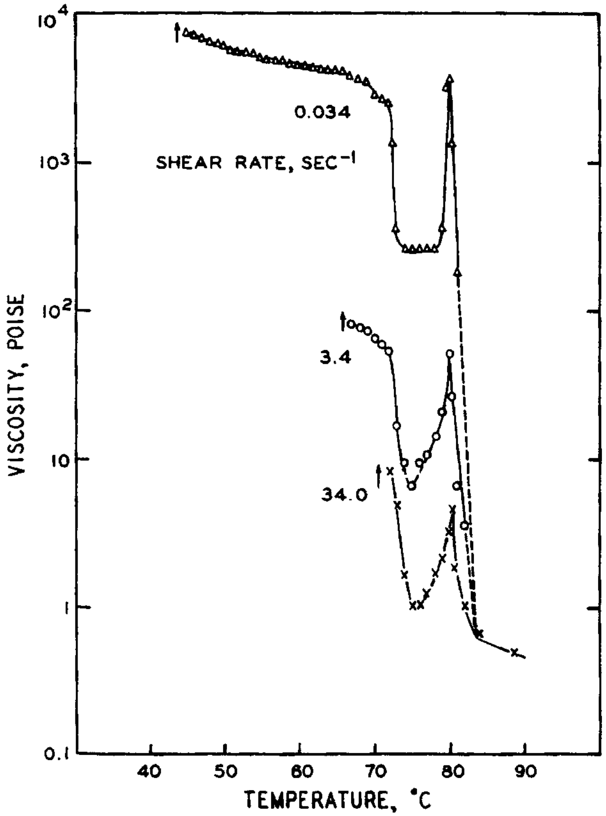
VISCOSITY CHANGE WITH TEMPERATURE
97.8% CHOLESTERYL MYRISTATE



rates as a continuous function of temperature. Thus tests were made on ester blends while transcending the temperatures for the characteristic transitions. All the thermodynamic transitions were readily observed rheologically at all shear rates and the characteristic flow behavior was detailed for each state. The viscosity breaks are more gradual as acetate concentration is increased although some curvature is observed on the smectic side of the cholestric transition for even the purest myristate yet tested[11]. The rheologically-observed transitions agree closely with those measured independently by differential scanning calorimetry[27]. This means that orientation forces in shear do not appreciably alter the thermodynamic order. Viscosities for both high and low molecular weight esters have been shown to be close to 22 centipoise at 117 °C[6]. This is in agreement

FIGURE 3

VISCOSITY CHANGE WITH TEMPERATURE
97.0% CHOLESTERYL MYRISTATE
3.0% CHOLESTERYL ACETATE



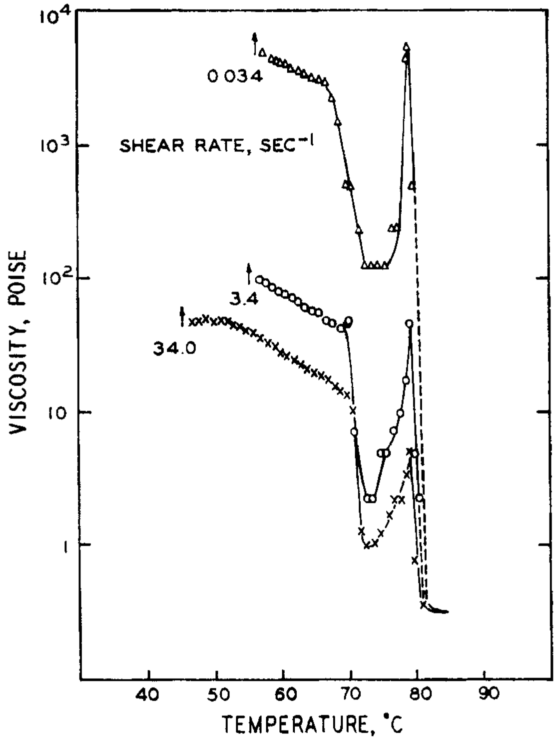
with extrapolation of data obtained here on ester blends. The kinematic and absolute viscosities for the isotropic states appear to be constant, within precision of present measurements, for the pure ester series above acetate through stearate and for the blends studied here. Importantly, all the esters are found to be Newtonian in the isotropic state over the measured shear rate ranges 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[6]. The observed Newtonian flow for the isotropic liquid is meaningful since x-ray studies show that molecules of cholesteryl esters in this state are extended, indicating the potential for anisotropic behavior[29]. No flow activation energies were calculated because of (1) the short temperature ranges involved and (2) changes in the

FIGURE 4

VISCOSITY CHANGE WITH TEMPERATURE

94.2% CHOLESTERYL MYRISTATE

5.8% CHOLESTERYL ACETATE



systems possible over the mesophase temperature range. Some values have been previously reported[11].

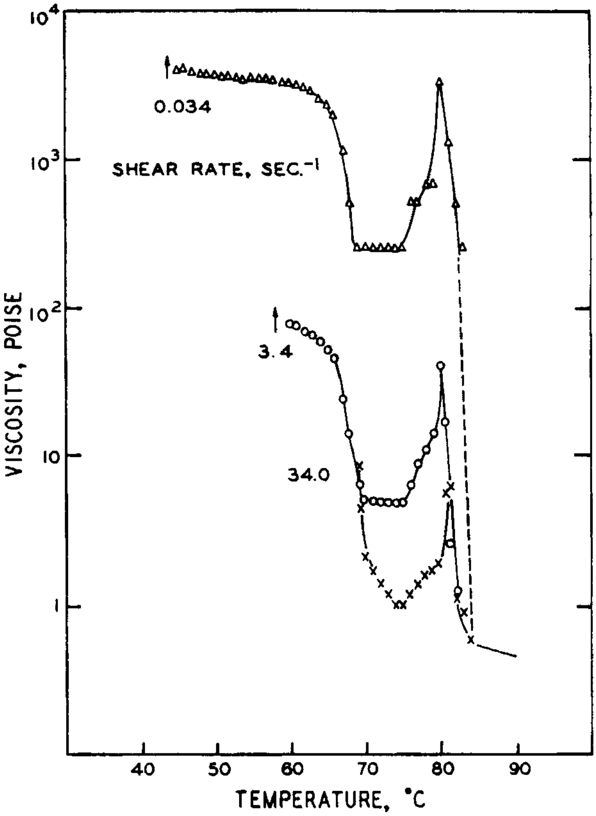
The cholesteric-isotropic transition was measured rheologically at five myristate concentrations of 78.1 mole % and above. Except for the lowest concentration, the transition temperature was invariant at 83 °C ± 1 °C, equivalent to the value for the pure myristate and for tests made by calorimetry, see Table I. The 78.1% myristate sample had a 5 °C lower transition. Similarly, the viscosities for all blends studied were equivalant in the isotropic state and equal to that for the pure myristate melt. The purest ester studied here, however, gave slightly higher smectic and isotropic viscosities than the earlier myristate report[11].

The viscosity results on the other transitions correlate very well with the

FIGURE 5

VISCOSITY CHANGE WITH TEMPERATURE

91.4% CHOLESTERYL MYRISTATE
8.6% CHOLESTERYL ACETATE



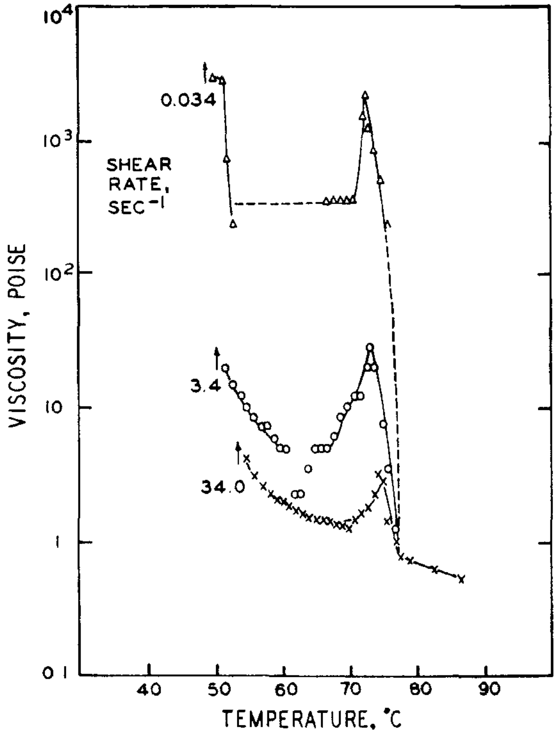
phase diagram as determined from DSC results in that the isotropic-cholesteric transition temperature remained constant, the cholesteric-smectic transition temperature decreased with decreasing myristate composition and indicating the apparent disappearance of the smectic phase in blends of less than 78% myristate. The sharp viscosity changes observed at the smectic-cholesteric and cholesteric-isotropic transitions correspond to unusually-small first-order transitions of 0.5 and 0.4 calories/gram for the pure myristate or only about 2% of normal fusion heats[26]. The isotropic transition heat is independent of composition. The smectic-cholesteric transition heat decreases with acetate content, vanishing near 78% myristate. The isotropic-cholesteric transition is characterized by a sharp increase in viscosity followed by an immediate viscosity drop for the rest of the cholesteric temperature range. The cholesteric-smectic transition on cooling is noted by another sharp rise in viscosity but followed by a leveling

FIGURE 6

VISCOSITY CHANGE WITH TEMPERATURE

78.1% CHOLESTERYL MYRISTATE

21.9% CHOLESTERYL ACETATE



off or continued slight increase in viscosity throughout the smectic phase followed by the very sharp, indefinitely-high increase in viscosity as the sample solidifies.

The heating cycle during continuous shear was difficult to control. Observations in two runs, however, were equivalent to the cooling studies except that they did not indicate the very sharp rise and fall of viscosity at the cholesteric-isotropic transition. This maximum is found to be unstable even in the cooling mode. When this state was kept at nearly constant temperature, ± 0.1 °C, under continuous shear, the viscosity was found to decrease with time. The peak also decreases markedly with shear rate, being eliminated at the highest rates. Others have found the viscosity spike is highest and narrowest at lowest shear rates, reportedly due to a dynamic focal-conic turbulence[22] , The changes are within a relatively large envelope shown in the figures 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[28] . This is not true, as has been also pointed out by Lawrence[9]. The maximum is rather a property of the transition. Features of this type have been documented and published[9,17,28] . For several single esters of cholesterol, the viscosity peak at the isotropic transition is reportedly symmetric. For neat esters, the viscosity maximum is sharp, extending only over about 2°C as demonstrated with the propionate[8,9], butyrate[8], myristate[11], and ethyl carbonate esters[8]. Most previous reports of the maximum have been made in capillaries with the inherent limitation of measurements at discrete temperatures and with inhomogeneous shear fields.

The figures indicate that there is a slight decrease in peak viscosity as the myristate content is reduced. At higher shear rates and acetate concentrations a broader viscosity maximum is also observed. The blends thus exhibit a greater artificial similarity to nematic mesophases as conjectured earlier[28] . For most samples, there was a slight break in viscosity on the cool side of the isotropic liquid-cholesteric transition. A similar break was found in the DSC trace at the same temperatures inferring a textural change measured by the two techniques. The broader viscosity peak and break are readily observable only when virtually all the shear dependence of viscosity has been sheared out. Independent studies on the myristate ester suggest that the broad peak and break observed at high shear may be due to the homeotropic texture which involves formation of smaller structures about 500 Å in size as measured by light scattering[30]. Independently, normal force measurements have been used to calculate the size of tumbling aggregates in a shear-generated homeotropic texture. The size estimate here is 500 Å and less[23]. The concentration of aggregates might be estimated by the Einstein equation which has only slightly different constants for aggregates of different geometry.

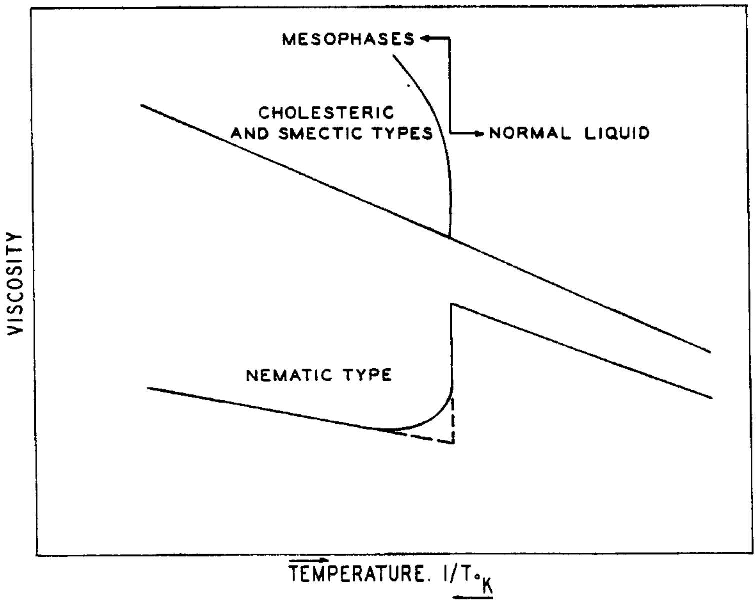
The mechanism for shear thinning in the cholesteric state has been discussed for another multicomponent ester system. With increasing shear it is suggested that first an orientation of rod-like helical arrays occurs (tiltable granjean textures) followed at higher shear by a partial break-up of the helices providing the blue color of the homeotropic cholesteric texture[22,24,31]. In this regard it is interesting to note that it has been suggested that the homeotropic texture is unstable but may be induced by shear[23]. This is consistent with the appearance of the broad peak at high shear and near the upper temperatures limit of the cholesteric mesophase, where indeed the homeotropic texture is expected.

True viscosities for the cholesteric mesophase, free of the peak near the isotropic transition, are more readily observed in the blends because of mesophase existence over a broader temperature range. The cholesteric viscosities are hypersensitive to shear but possibly independent of composition with viscosities virtually the same within precision at the same shear rates for all tested compositions. This is a very interesting finding. Thus, rheologically, as well as thermodynamically, these esters see one another as equivalent, verifying the cholesteric mesophase being due solely to the organization of the steroid moiety.

For the binary systems studied here, the smectic mesophases also have similar viscosities when compared at the same temperature and shear rate. The precision for this conclusion is not high. The viscosity changes for the smectic mesophase with composition are nonetheless small to non-existent, particularly compared

FIGURE 7

CHARACTERISTIC FLOW OF MESOPHASE TYPES



to the dramatic smectic mesophase viscosity changes with shear rate. This remarkable conclusion was also indicated above for the cholesteric mesophase. Smectic viscosity data are equivalent when compared at the same temperature rather than at equal temperatures below the cholesteric-isotropic transition.

It has been previously shown that the viscosity of the neat acetate depends markedly on purity[4,6–8]. This result differs from the blends studied here. This is because the acetate is monotropic and readily crystallizes. This means that it is not a change in mesophase viscosity per se, but the effect of impurity on suppression of the crystallization and the consequent measurement of a slurry viscosity rather than a true mesophase viscosity. It is also possible that continuous, lamellar shear reduces crystal supercooling with the disappearance of monotropic behavior[4]. Near equilibrium crystallization, without major undercooling in the predominantly myristate systems, may be noted at the lowest temperatures in the figures. 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. The rheological transition in general is lower than the corresponding values by calorimetry. This may be due to minor supercooling. A minor shear reduction of the equilibrium transition temperature is also a possibility. Nonetheless, the transition is higher (less supercooling) than that observed calorimetrically without shear[27].

The minimum measured cholesteric mesophase viscosity is located near the extension of the viscosity vs temperature plot for the isotropic phase. It may therefore be postulated that a minimum viscosity for the cholesteric mesophase has been reached at only moderate shear rates and stress and that the high-shear limiting viscosities for the cholesteric mesophase can thus be closely predicted by an extrapolation to lower temperature of viscosities for the isotropic liquid. This same limit likely holds for the smectic phase, but higher shear rates and stresses are required. Limiting high shear viscosities for cholesteric and smectic mesophases have both been reached at shear stresses 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 $\leq 10^2$ dynes/cm^2 in shear stress.

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

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 mesophase must be due in part to orientation and then partial distruction of the structures. Thus there are at least two rheological features distinguishing nematic and cholesteric mesophases. The former are lower in viscosity than the isotropic state and the structures have not as yet been broken by high lamellar shear. The cholesteric structures, on the other hand, cannot be readily unscrewed by shear (indeed the pitch is not changed) yet they are likely partially destroyed by shear leading to the blue homeotropic phase and a viscosity similar to the isotropic state[22,23,27,31]. This conclusion also comes from previously published photomicrographs by these workers for cholesteryl myristate in the sheared and unsheared state[11].

The results of this study also indicate that viscosities for the cholesteric mesophase are relatively low compared to the smectic mesophase and thus can be readily distinguished in the same system. The viscosities for both mesophases are markedly shear dependent. The smectic and perhaps the cholesteric mesophase may exhibit a yield stress. They both fall, however, in an envelope of values exceeding the isotropic state, see last figure. This figure schematically displays the generalized behavior for compounds exhibiting a single mesophase. In addition, compounds which exhibit a nematic mesophase generally have lower viscosities and flow activation energies for both the isotropic and mesophase regions. This is indicated schematically in the last figure. The documenting data are given in this and earlier papers in this publication series.

Quite another behavior is of course observed for the nematic type of liquid crystal. Viscosity tests thus represent a simple, sensitive, and definitive method for distinguishing smectic, cholesteric and nematic mesophases.

Rheological documentation of mesophase-mesophase transitions of any type are relatively rare[3]. Recently, however, a number of interesting studies on mesophases and their transitions have been developed by a variety of techniques which provide rheological data such as dynamic tests, low resolution nuclear magnetic resonance, and acoustical and ultrasonic methods.[32-38] The present study represents the second set of continuous shear viscosity data to be reported for blends of cholesteryl esters. The sum of recent studies in the field of mesophase rheology, cited herewith, possess a scope and understanding which more than doubles the total information available up to the time of our 1968 review[3]

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