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Viscosities of Cholesteryl Myristate, Palmitate and Oleate in the Isotropic, Cholesteric and Transition States with and without the Addition of Higher Alkanols

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The viscosities of cholesteryl myristate (ChM), cholesteryl palmitate (ChP) and cholesteryl oleate (ChO) were measured with a cone-plate viscometer at various shear rates with continuous heating. After a rapid decrease near the smectic–cholesteric transition temperature, the viscosities decreased gradually in the cholesteric and isotropic phases, with a peak at the cholesteric-isotropic transition. The viscosity peak temperature agrees reasonably well with the values obtained by differential scanning calorimetry (DSC) and polarized light microscopy. From the shear rate *vs.* shearing stress relations at various temperatures, it was concluded that the flow in the isotropic phase was Newtonian, while the flow in the cholesteric phase was non-Newtonian. With respect to the cholesteric-isotropic transition temperature, the effect of alkanols on the viscosity of ChM was the same as that on the DSC curve. However, the viscosity *vs.* temperature curve showed a stronger transition peak than the DSC curve, in spite of the addition of alkanols. The change of ChM viscosity under stress was also followed at various temperatures; the "static viscosity" was obtained by extrapolation of the viscosity to zero time and the "kinetic viscosity" from the steady-state value under stress. Comparison between the viscosity measured with continuous heating and the kinetic viscosity confirmed the validity of the former method, especially in the isotropic and cholesteric–isotropic transition states.

Keywords——liquid crystal; cholesteryl myristate; cholesteryl palmitate; cholesteryl oleate; viscosity; cholesteric phase; phase transition temperature; nonanol; dodecanol; activation energy

Introduction

Cholesteryl myristate, palmitate and oleate (ChM, ChP and ChO, respectively) have solid, smectic, cholesteric and isotropic phases, which occur in that order as the temperature increases.[2,3] The addition of a small amount of a soluble compound (lower alkane or alkanol) remarkably changes the structures of liquid crystal phases, as previously studied by us from a thermodynamic standpoint using gas-liquid chromatography[2,3] and differential scanning calorimetry.[4]

In this work, we measured the viscosity of ChM, ChP and ChO in the isotropic and cholesteric phases, as well as in the transition region between them with and without alkanes and alkanols, in the expectation that the structural changes of the liquid crystal phases due to the addition of solute might affect the flow properties.

Experimental

Materials

Liquid Crystal Substances: ChM, ChP and ChO were obtained from Tokyo Kasei Kogyo Co., Ltd. and were used after several recrystallizations from ethanol.

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[1] Location: *Tanabe-dori, Mizuho-ku, Nagoya, 467, Japan.*
[2] I. Miyata and H. Kishimoto, *Yakugaku Zasshi*, **98**, 689 (1978).
[3] I. Miyata and H. Kishimoto, *Yakugaku Zasshi*, **98**, 1629 (1978).
[4] I. Miyata and H. Kishimoto, *Chem. Pharm. Bull.*, 27, 1412 (1979).

Solutes: *n*-Nonane (special grade for gas chromatographic use), *n*-nonanol (special grade) and *n*-dodecanol (special grade) were obtained from Tokyo Kasei Kogyo Co., Ltd. *n*-Nonanol was used after vacuum distillation and *n*-dodecanol was used after two recrystallizations from the molten state.

Apparatus

Cone-and-plate Viscometer: An E-type viscometer from Tokyo Keiki Co., Ltd. was used. The cone angle and the radius of the rotator were 3° and 1.4 cm, respectively.

Preparation and Filling of the Sample——Mixtures of liquid crystal and solute were prepared as described in the previous paper.[4] About 0.6—0.7 g of sample, *i.e.*, a liquid crystal substance or its mixture with a solute, in the isotropic state (see Fig. 1) at *ca.* 361, 358 and 328 K for ChM, ChP and ChO, respectively, was placed in the space between the cone and plate of the viscometer, the temperature of which was controlled by the circulation of thermostated water through a jacketed casing under the plate. The temperature was determined with a mercury thermometer (±0.1 K) inserted in the thermally insulated drain pipe for the thermostated water, at 20 cm from the exit of the jacketed casing.

Results and Discussion

Phase Diagrams

Fig. 1 shows the transition paths and temperatures for the three liquid crystal substances, which were measured previously[3,4] by polarized light microscopy (PLM) with a high-grade hot stage (Mettler FP5, FP52) and by differential scanning calorimetry (DSC) using a TG–DSC unit (Hyojungata, Rigakudenki Co., Ltd.).

Various lines of evidence indicate the transitions designated by the arrows in Fig. 1 to be of first-order,[5-7] although several of these transitions, *e.g.*, the transition between the

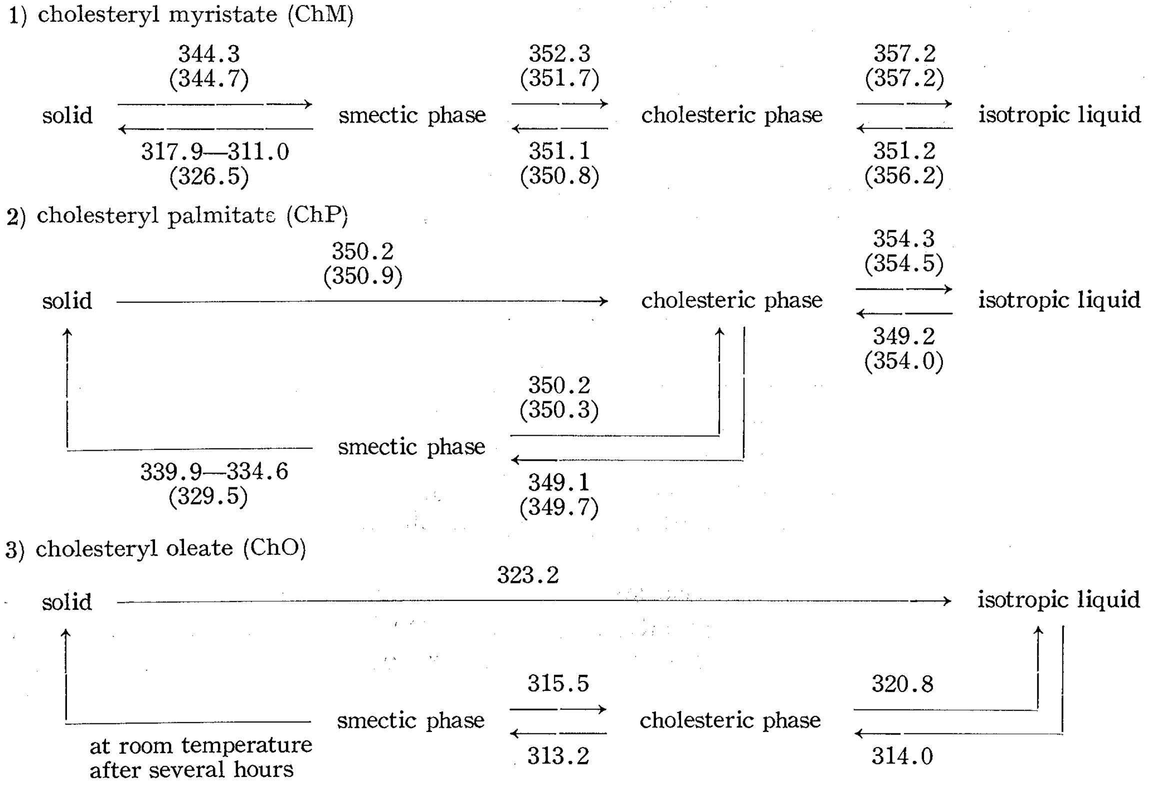

Fig. 1. Transition Paths and Temperatures for the Three Liquid Crystal Substances

Right-and left-pointing arrows designate the heating and cooling processes, respectively. Figures on the arrows show the transition temperatures (degrees Kelvin) measured by microscopic observation[3] and figures in brackets show the transition temperatures defined as the peaks of the DSC curves.[4] Supercooling occurs at the transition by cooling.

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5) E.M. Barrall, II, R.S. Porter, and J.F. Johnson, *J. Phys. Chem.*, **70**, 385 (1966).
6) E.M. Barrall, II, R.S. Porter, and J.F. Johnson, *J. Phys. Chem.*, **71**, 895 (1967).
7) G.J. Davis, R.S. Porter, J.W. Steiner, and D.M. Small, *Mol. Cryst. Liq. Cryst.*, **10**, 331 (1970).

solid and cholesteric phases of ChP, are irreversible (or monotropic). In a reversible (or enantiotropic) transition, the temperature determined by the heating process can be considered to be more valid than that determined by the cooling process, since some degree of supercooling usually occurs in the cooling process. The relatively good agreement between the values determined by microscopic observations and DSC in Fig. 1 confirms the validity of the heating process. Of course, the determination of a monotropic transition temperature by heating will be similarly valid.

Viscosity Measurements of Pure ChM under Various Heating Conditions

Viscosity Measurement with Continuous Heating——After filling the viscometer, ChM was rapidly cooled until it solidified into the smectic state and was then kept at *ca.* 348 K for about 1 hr for ageing without shear. Subsequently, it was heated at a rate of 0.5 K min^{-1} to nearly 351 K, at which point the fluidity of the sample increased abruptly, becoming measurable. In this temperature range (348—351 K), slight stress had been intermittently applied to the ChM to examine the possibility of viscosity measurement with this apparatus. From *ca.* 351 K, the viscosity of ChM heated at a rate of 0.5 K min^{-1} with a constant shear rate of 10 s^{-1} was measured and plotted (triangles) on a logarithmic scale against the reciprocal of absolute temperature (Fig. 2).

Comparing the viscosity data in Fig. 2 with the DSC curve (below), the initial rapid decrease of viscosity reflected the transition (352 k) from the smetic to the cholesteric phase and the intermediate peak reflected the transition (357 K) from the cholesteric to the isotropic phase.

Viscosity Measurement without Temperature Change——The property observed by the temperature-scanning measurement in a finite time is usually not strictly an equilibrium state function, but depends upon the ageing of the material due to its imperfect relaxation. In a system under a shearing force, there is also the possibility that a steady-state depending on stress or shear may exist besides the usual static equilibrium state. Thus, we carried out the following experiments.

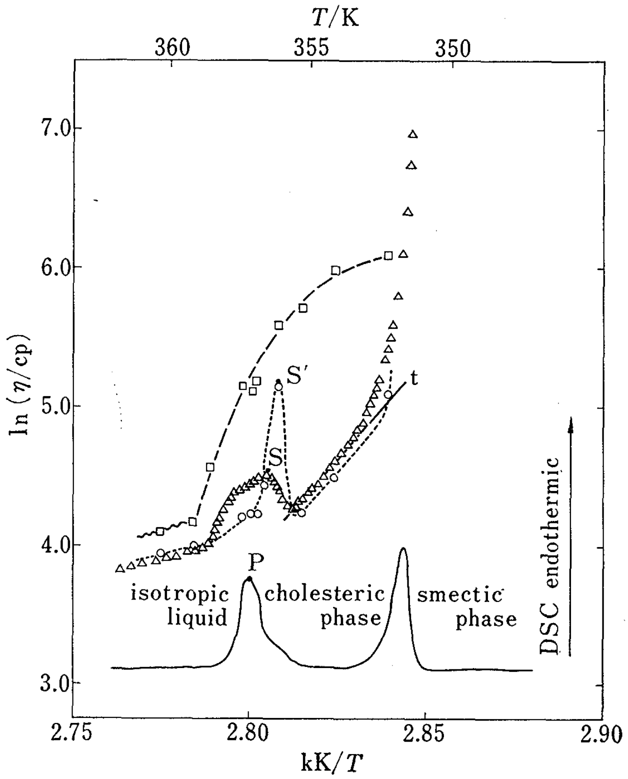

Fig. 2. ChM Viscosities Measured by Various Procedures, and the DSC Curve *vs.* Reciprocal of Temperature

Upper Figure : Viscosity plots at a shear rate of 10 s^{-1}
△ : viscosity with continuous heating at 0.5 K min^{-1},
□ : viscosity extrapolated to zero time at constant temperature (static viscosity),
○ : steady-state viscosity at constant temperature (kinetic viscosity).
Lower Figure: DSC curve at a heating rate of 2.5 K min^{-1}
S, S' and P show the summits of curves (see the text), and line t is the tangent drawn on the viscosity curve with continuous heating (see the text).

In contrast to the case of measurement with continuous heating, ChM, which had been placed in the viscometer in the isotropic state, was cooled to a specified temperature and kept there for 1 hr without shear for thermal equilibration. With a constant shear rate of 10 s^{-1} and at same temperature, the viscosity was measured. At any temperature, the measured viscosity first decreased exponentially and finally approached a definite steady-state value. The viscosity obtained by extrapolation of the exponentially decreasing viscosity plots to zero time will be called the "static viscosity" by analogy with the so-called "static friction" in mechanics. The finally approached value of viscosity depends on the applied shear rate as well as the temperature, and will be called the "kinetic viscosity" by analogy with "kinetic friction" in mechanics. The static and kinetic viscosities at various temperatures are plotted in Fig. 2 (squares and circles, respectively).

Because of the difficulty in measuring the rapidly changing viscosity in the initial stage after the application of stress to ChM, the extrapolated static viscosity may not be sufficiently accurate for analysis. For the present, we can only say qualitatively that the static viscosities plotted on a logarithmic scale against the reciprocal of temperature show a sigmoidal declining curve (broken curve) in the cholesteric phase followed by a slow linear decline (wavy line).

Throughout the cholesteric and isotropic phases, the plot of kinetic viscosity shows a gentle declining curve (dotted in Fig. 2) with a sharp peak at the cholesteric–isotropic transition. The presence of a sharp transition peak suggests the occurrence of some complex structure, although it is not clear whether it consists of a fine heterogeneous dispersion of two co-existing phases similar to an emulsion or a homogeneous gel structure resulting from the imperfect breakdown of the cholesteric phase.

Discussion of the Viscosity Plot with Continuous Heating

Compared with the sharp peak of the kinetic viscosity plot, the viscosity plot obtained with continuous heating shows a rather broad hump at the cholesteric–isotropic transition, although the summits of both plots seem to coincide with respect to temperature. The broadness of the latter plot suggests a delayed response of the sample to the temperature increase, especially on the higher temperature side of the transition. The difference between the viscosity with continuous heating and the kinetic viscosity in the cholesteric phase, especially in the lower temperature region, seems to result from the "immaturity" of the state probed by the former viscosity measurement.

In spite of the broadness of the transition peak and the immature value in the cholesteric phase, the viscosity plot with continuous heating seems a useful and easy means to examine the transition temperature under stress and the viscosity–temperature relationship in the isotropic phase. The transition temperature under stress showed only a slight difference from the transition peak of the DSC curve, as shown in Table I. This might result from differences in the experimental conditions, *e.g.*, heating rate or the kind of containing vessel, or simply from error in measuring the temperature of the sample in the viscometer. Before the cholesteric–isotropic transition, the viscosity curve with continuous heating runs parallel to the kinetic viscosity curve with the same tangent, as shown by line t in Fig. 2. In the higher temperature region of the isotropic phase, both curves coincide, giving a linear relation of logarithmic viscosity *vs.* reciprocal of temperature. Thus, we can approximate the activation energies of viscous flow, $U^{\ast}$, from the tangents of the linear plots in the cholesteric and isotropic phases, according to the following empirical equation:

$$\ln \eta = \ln B + U^{\ast}/RT \tag{1}$$

where B is a constant, R is the gas constant and T is absolute temperature. The transition temperature under stress and the activation energy of flow of ChM are shown in Tables I and II.

The molecules of ChM at ground level in the cholesteric phase seem to be constrained in energy terms more strongly than in the isotropic phase, although the absolute value $U^{\ast}$ in the isotropic phase is still large compared with the value of common liquids, *e.g.*, 12.97 kJ mol^{-1} (at 50—100°) for water, and 8.66 kJ mol^{-1} (at 0—100°) for toluene.[8)]

The tangent for the activation energy in the cholesteric phase can be approximately drawn, as shown in Fig. 3, even without comparison with the kinetic viscosity data. The

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8) T. Nakagawa, "Rheology," in Japanese, 2nd ed., Iwanami Book Co., Tokyo, 1978, p. 118.

Table I. The Cholesteric-isotropic Transition Temperatures Measured by Various Methods

Liquid crystal substance	Process	PLM[a)]	DSC[b)]	Viscometry[c)]
Cholesteryl myristate	Heating	357.2K	357.2K	356.6K
	Cooling	351.2K	356.2K	—
Cholesteryl palmitate	Heating	354.3K	354.5K	353.7K
	Cooling	349.2K	354.0K	—
Cholesteryl oleate	Heating	320.8K	—	321.2K
	Cooling	314.2K	—	—

[a)] Polarized light microscopy. [b)] The peak temperatures (P) on the differential scanning calorimetry curve.
[c)] The peak viscosities (S) with continuous heating.

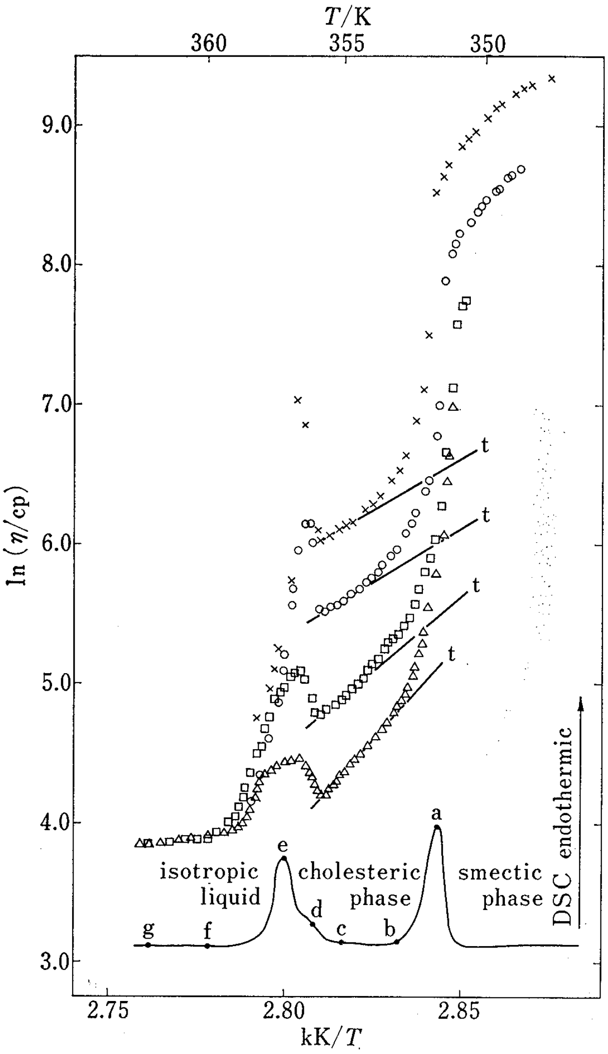

Fig. 3-a. ChM Viscosities Measured at Various Shear Rates and the DSC Curve *vs.* Reciprocal of Temperature

Upper Figure : Viscosity plots with continuous heating at 0.5 K min^{-1}

Shear rate : 1 s^{-1}(×), 2 s^{-1}(○), 5 s^{-1}(□), and 10 s^{-1}(△).

The tangents for the activation energies in the cholesteric phase are marked with t's.

Lower Figure : The same DSC curve as in Fig. 2

Temperatures a, b, c, d, e, f, and g on the curve are 351.5, 353, 355, 356, 357, 359, and 362 K, respectively.

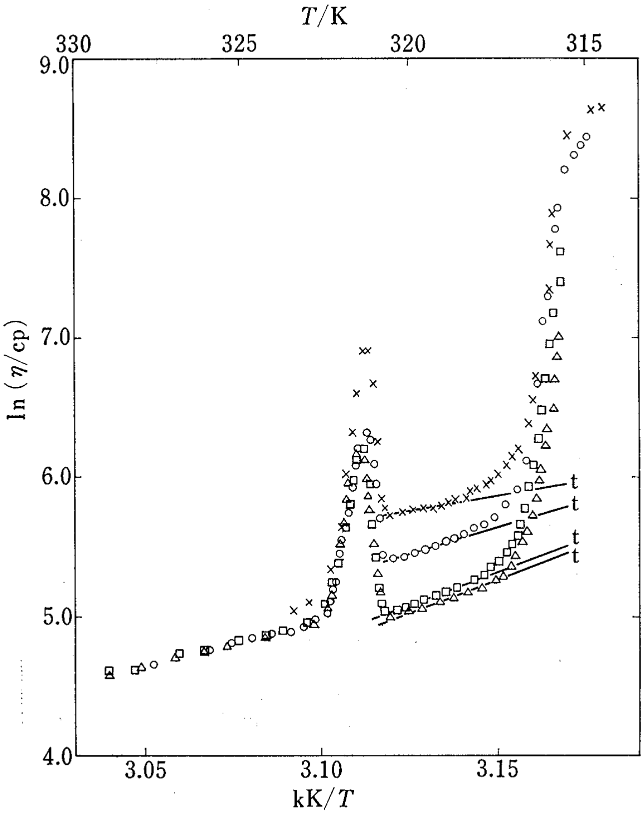

Fig. 3-b. ChO Viscosities Measured at Various Shear Rates *vs.* Reciprocal of Temperature

Conditions and symbols are the same as in Fig. 3-a.

TABLE II. Activation Energy of Flow

Liquid crystal substance	Shear rate/s^{-1}	$U^{\ast}/\mathrm{k}J\ \mathrm{mol}^{-1}$	
		Cholesteric phase	Isotropic liquid
Cholesteryl myristate	1	123.8 (355K)	36.7(360K)
	2	129.3	
	5	181.9	
	10	235.6	
Cholesteryl palmitate	1	124.7(352K)	46.2(357K)
	2	— —	
	5	— —	
	10	207.9(352K)	
Cholesteryl oleate	1	36.7 (319K)	52.7(325K)
	2	60.6	
	5	72.8	
	10	78.7	

activation energies and cholesteric–isotropic transition temperatures of ChP and ChO, which were estimated simply from the viscosity plot with continuous heating, are shown in Tables II and I, respectively. The situations for ChP and ChO are similar to that for ChM.

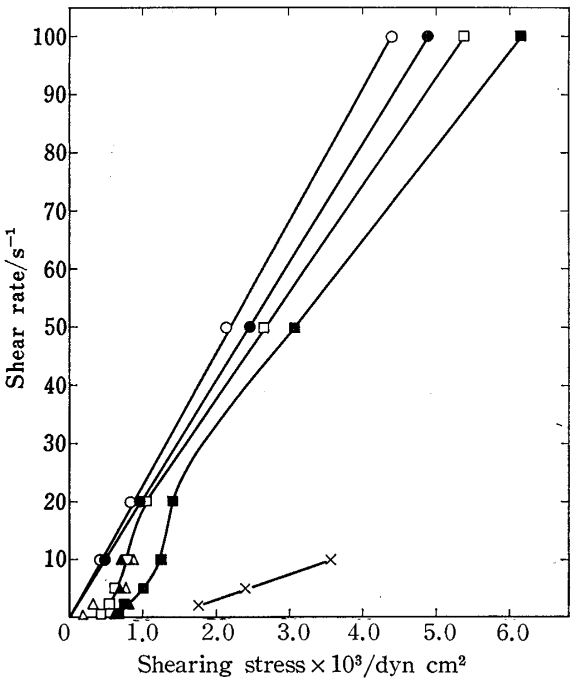

Fig. 4. Shear Rate *vs.* Shearing Stress Relations for ChM

× : in the smectic-cholesteric transition region (a),
■ : in the cholesteric phase (b),
□ : in the cholesteric phase (c),
▲ : in the cholesteric-isotropic transition region (d),
△ : in the cholesteric-isotropic transition region (e),
● : in the isotropic liquid (f),
○ : in the isotropic liquid (g).

The letters in parentheses correspond to the letters on the DSC curve in Fig. 3-a and show the temperatures at which the plots denoted by the above symbols were obtained.

Viscosity Measurements of Pure Liquid Crystal Substances at Various Shear Rates

For pure ChM, ChP and ChO, the viscosities were measured continuously with heating at various shear rates, as shown in Fig. 3; the plot of ChP is omitted since it overlaps that for ChM. The viscosity at the cholesteric–isotropic transition became higher with lower shear rate, while the transition peak scarcely shifted on the temperature abscissa. Higher viscosity was observed in the cholesteric phase with lower shear rate, while the viscosity in the isotropic state did not depend on the shear rate.

First, we shall consider the viscosity of the cholesteric phase at various shear rates. As shown in Fig. 3 and Table II, the activated state of flow is higher in terms of $U^{\ast}$ with higher shear rate, while the viscosity itself is lower. These opposing tendencies cannot be explained by the simple application of Eq. (1). According to Eyring *et al.*,[9] the constant B in Eq. (1). can be divided into two terms, *i.e.*, a constant term and an entropy term, as follows:

$$\ln B = \ln K - S^{\ast}/R \qquad (2)$$

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[9] S. Glasstone, K.J. Laidler, and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Company Inc., New York, 1941, p. 477.

where K is a constant and $S^{\ast}$ is the activation entropy of viscosity. Thus,

$$\ln \eta = \ln K + U^{\ast}/RT - S^{\ast}/R \tag{3}$$

The above-mentioned trends of $U^{\ast}$ and viscosity itself require that $S^{\ast}$ at lower shear rate should be lower than $S^{\ast}$ at higher shear rate, or that the activated state of the cholesteric phase at lower shear rate should have a higher order of structure than that at higher shear rate. Based on the lower $U^{\ast}$ and $S^{\ast}$ of the cholesteric state at lower shear rate and higher $U^{\ast}$ and $S^{\ast}$ at higher shear rate, we may suppose that the kinetic unit (*e.g.*, swarm[2,3)]) of the cholesteric phase forms a network structure by activation at lower shear rate and a "completely broken" structure at higher shear rate.

On the other hand, the higher viscosity peak of the cholesteric–isotropic transition at lower shear rate implies that the structure at this transition has a certain network linkage, which can be broken under stress. This implication supports a homogeneous gel structure, rather than a heterogeneous emulsion–type dispersion. Even if the transition structure is of the latter type, the dispersed droplets might be connected with each other, forming a network. By analogy with the above-mentioned behavior of the cholesteric phase under stress, the supposed network structure under stress at the cholesteric–isotropic transition may be similar to the network structure of the activated state of the cholesteric phase at flow, although it is, so to speak, swollen by the isotropic phase.

Rearranging the data plotted in Fig. 3-a and adding the viscosity data with various shear rates at various temperatures, we obtained the relation of shear rate *vs.* shearing stress for ChM at various temperatures corresponding to various phases. As shown in Fig. 4, the flow in the isotropic phase is Newtonian, but the flow in the cholesteric phase is non-Newtonian or plastic, having a definite yield value of stress, which supports the network structure

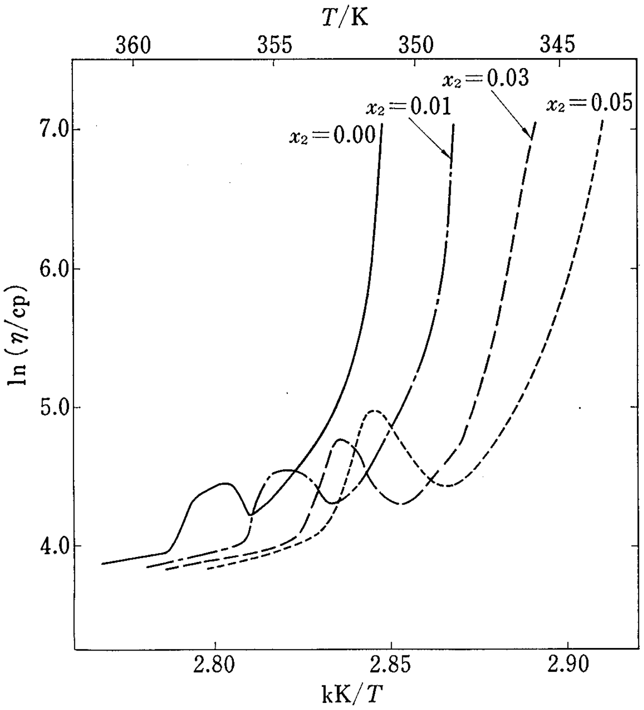

Fig. 5-a. ChM Viscosity *vs.* Reciprocal of Temperature Relations with Various Amounts of *n*-Nonanol

Measured data are replaced by smoothed curves. The value at the top of each curve denotes the mole fraction of *n*-nonanol.

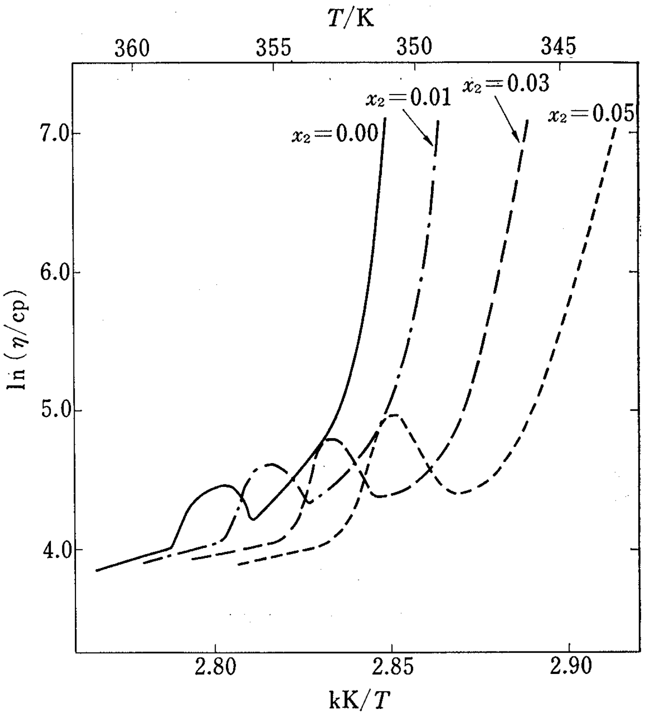

Fig. 5-b. ChM Viscosities *vs.*Reciprocal of Temperature Relations with Various Amounts of *n*-Dodecanol

Measured data are replaced by smoothed curves. The value at the top of each curve denotes the mole fraction of *n*-dodecanol.

proposed above in the discussions of flow in the cholesteric phase. Near the cholesteric–isotropic transition temperature, the flow properties became complex. For ChP and ChO, similar flow properties were found.

Effect of Solute on the Viscosity of ChM

We carried out similar viscosity measurements with continuous heating at the same shear rate of 10 s^{-1} with various amounts of solute in ChM. If such a volatile solute as *n*-nonane (b.p. 424 K) was added, however, we could not obtain a viscosity *vs.* temperature curve comparable to the DSC plot with respect to the cholesteric–isotropic transition (357 K), probably due to the evaporation and loss of *n*-nonane from the system at higher temperature. By inspection of Fig. 5, where the results with the addition of *n*-nonanol (b.p. 486.7 K) and *n*-dodecanol (b.p. 426.7 K (25 mmHg)) are shown as viscosity *vs.* reciprocal of temperature curves, it was concluded that the presence of a solute lowers the viscosities of the isotropic and cholesteric phases and the transition temperature. The viscosity peak at the cholesteric–isotropic transition seems to become higher than expected from the increase of viscosity due to the lowered transition temperature. At least, it seems clear that the transition viscosity peak sharpened with the addition of solute, in contrast to the flattening of the DSC transition peak. This sharpening of the viscosity peak measured with continuous heating suggests that the addition of solute made the motion of ChM at a molecular level easier, and reduced the already mentioned delay of viscosity response to heating at the transition. The activation energy of flow in the isotropic phase was almost unchanged. A similar situation seems to exist in the cholesteric phase with the addition of solute.

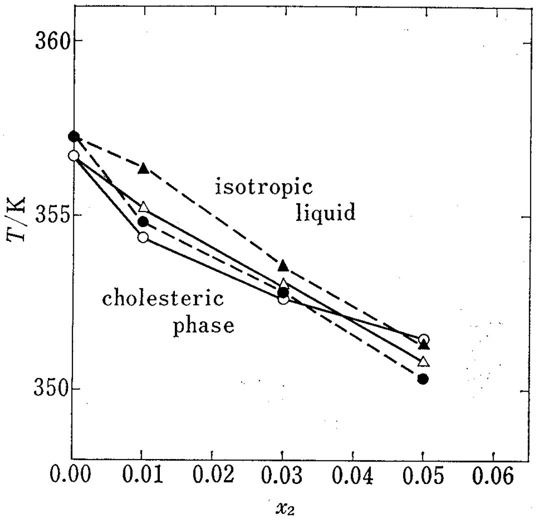

Fig. 6. Cholesteric-isotropic Transition Temperature of ChM *vs.* Mole Fraction of Solute

Solute: *n*-nonanol (circles) and *n*-dodecanol (triangles). Measurement: viscosity (open symbols) and DSC (solid symbols).

	Viscometry	DSC
n-nonanol	—○—	···●···
n-dodecanol	—△—	···▲···

The temperatures of the cholesteric–isotropic transition, defined as the peak positions on the logarithm of viscosity *vs.* reciprocal of temperature curve and the DSC curve, S and P in Fig. 2, respectively, are plotted in Fig. 6 against the mole fraction of solute in the ChM–solute system. Both kinds of transition temperature (from viscosity and DSC measurements) agreed reasonably well. This means that the cholesteric–isotropic transition is fundamentally the same, in spite of the difference of properties, *i.e.*, mechanical or thermal, measured. It was concluded that viscosity measurements with continuous heating can conveniently be used to determine the cholesteric–isotropic transition temperature in the presence or absence of a non-volatile solute, and reflect the flow properties of the liquid crystals at least qualitatively.