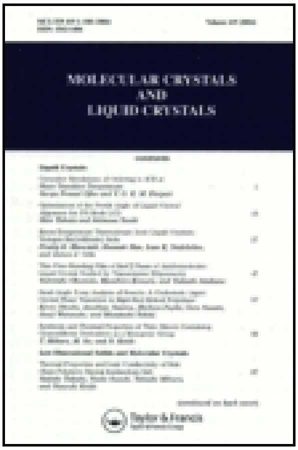

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Surface Tension of Cholesteric Liquid Crystals: Cholesteryl Myristate

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Abstract—It has been suggested that the surface region of ordered liquids and, in particular, liquid crystals may extend well into the bulk phase.[1] The surface tension of such materials could be expected to reflect changes in bulk properties and should be sensitive to mesophase transitions. In this study the surface tension of cholesteryl myristate was measured as a function of continuously varying temperature. On cooling into the cholesteric phase, the surface tension exhibits a steep rise of up to 10 dynes/cm and then falls back abruptly before the cholesteric-smectic transition. In the heating mode, the surface tension of the cholesteric phase was relatively independent of temperature. Similar anomalies which are dependent on the direction of thermal change have been reported for the viscosity of cholesteric esters.

Introduction

The surface tension of a liquid is the result of an unbalance of forces within a surface region which, in the classical view, is no more than a few molecular diameters in thickness. It has been suggested that the surface region of associated liquids may extend well into the bulk[1] and there is evidence that anomalies in the surface tension of water as a function of temperature are due to bulk structural changes.[2] The high degree of ordering characteristic of liquid crystals should make the surface tension very sensitive to bulk changes and such measurements may furnish some insight into the nature of the mesophase transitions.

Schwartz and Mosely[3] have determined the surface tension of the nematic liquid crystals *p*-azoxyanisole and *p*-azoxyphenetole. The surface tension of these materials increased linearly with decreasing temperature in both the isotropic and nematic phases but the slope was greater in the nematic phase. At the isotropic to nematic transition a slight break in the surface tension curve was observed. The present work was undertaken to determine the surface tension of the cholesteric phase. This was found to be much more complex than that of the nematic phase.

Surface tension measurements were made by the Wilhelmy slide method in the static mode. A detachment method is valid only if the surface reaches equilibrium very quickly[4] which is probably not the case for liquid crystals. Schwartz and Mosely[3] indicated that the ring detachment method could not be used for the smectic phase of *p*-azoxybenzoate because of the high viscosity in this phase. Also, the cholesteric phase is very sensitive to shear[5] and the act of detachment could cause reorientation of the surface structure. The Wilhelmy slide method is readily adapted to continuous measurement of surface tension as a function of temperature.

Cholesteryl myristate was chosen for these studies because the mesophase transitions are well defined and are thermally reversible. Extensive thermal and optical information for this compound are available in the literature.[6,7]

Experimental

APPARATUS

The surface tension apparatus is shown in Fig. 1. The sample cell was an 80 × 40 mm glass vial with a standard taper cover. Holes were cut in the cover to admit the Wilhelmy slide and the sample thermocouple. An aluminium furnace was wrapped with two nichrome heater windings overlaid with asbestos. The outer heater was controlled by hand adjustment of an autotransformer for coarse temperature control; the inner heater was connected to the temperature programming circuit of a DuPont 900 Differential Thermal Analyzer. At slow thermal rates, less than 0.15 degrees per minute, the sample temperature change was

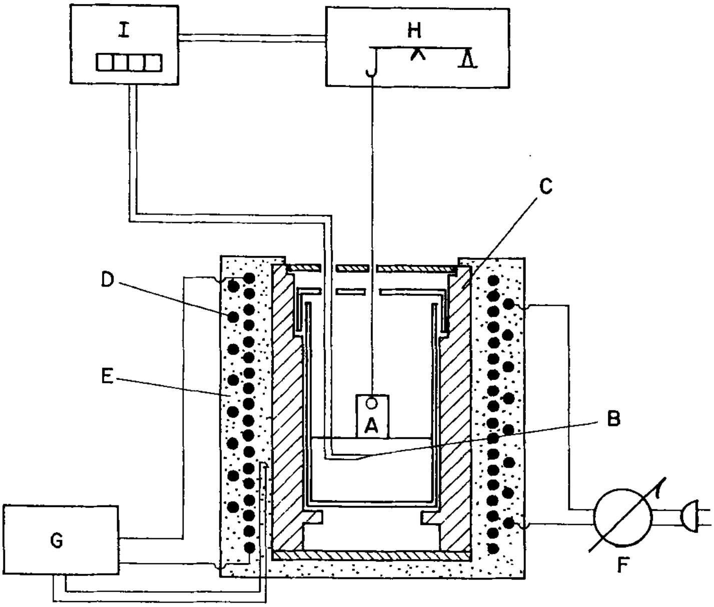

Figure 1. Surface tension apparatus. A, depolished platinum slide; B, sample thermocouple; C, furnace; D, heater windings; E, asbestos; F, autotransformer; G, temperature programmer; H, electrobalance; I, digital voltmeter.

nearly linear with the time but at faster rates the transition heats of the sample resulted in uneven temperature-time profiles.

A platinum sensor, 1 × 3 cm by .025 mm thick, was depolished over the lower 2.5 cm by air blasting with alumina. The slide was suspended from a Cahn RG electrobalance which maintained the bottom edge of the slide even with the liquid surface.

A stainless steel clad thermocouple, positioned just under the liquid surface a few millimeters from the slide, measured the sample temperature. The outputs from the electrobalance and the sample thermocouple were read at ten second intervals with a digital voltmeter and were recorded on punched tape. Conversion of the data to temperature and surface tension was done by computer.

The apparatus was checked by measuring the surface tension of benzene. The results shown in Fig. 2 are within 0.2% of literature values. The accuracy normally attributed to the Wilhelmy method is 0.1% but the present values were measured with a continuously varying temperature and are felt to be as good as can be expected under this condition.

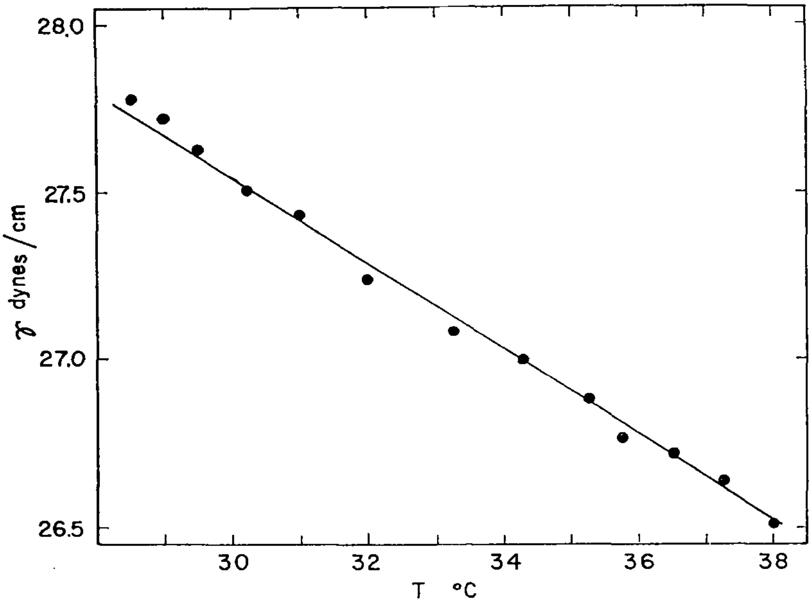

Figure 2. Surface tension of benzene. Points, experimental; line, calculated from literature values, *International Critical Tables*, Vol. IV, p. 454, McGraw-Hill Book Co., New York, 1928.

MATERIALS

Cholesteryl myristate, purchased from Aldrich Chemical Company, was recrystallized twice from ethanol and finally, in most cases, from a 4 : 1 acetone-benzene mixture. Prior to use it was pumped overnight in a vacuum desiccator with a liquid nitrogen trapped mechanical pump. The transition temperatures obtained by differential thermal analysis are listed in Table 1. These temperatures are lower than the literature values indicating some impurity. Thin layer chromatography showed only one spot but this is not conclusive since it is very difficult to separate neighboring ester in a homologous series.

Table 1 Transition Temperatures of Cholesteryl Myristate by Differential Thermal Analysis

Sample	Recrystallization Solvent	Transition Temperatures		
		T_1	T_2	T_3
I	Acetone-benzene	70.8	78.8	84.2
II	Acetone-benzene	70.8	78.8	84.2
III	Ethanol	69.5	78.4	83.5
Literature ref. 8		73.6	79.9	85.5
ref. 9		71	81	86.5

Results and Discussion

The procedure normally followed in these experiments was to heat the sample to a few degrees above the isotropic transition temperature, bring the platinum slide in contact with the surface and then set the temperature programmer to cool. After the temperature had dropped below the cholesteric-smectic transition the programmer was reversed and the sample was heated back to the isotropic state. At the end of a run the slide was withdrawn and inspected. In every run the liquid had wet the slide to the top of the depolished area.

The surface tension of cholesteryl myristate as a function of temperature for two thermal rates is shown in Figs. 3 and 4. The most remarkable feature of these studies was the large increase in surface tension on cooling into the cholesteric phase. This increase was observed in each of fourteen runs made with cholesteryl myristate. The surface tension maximum was dependent on the cooling rate and fell between 28 and 30.5 dynes/cm in all but one run. The exception was for the sample recrystallized only from ethanol. This sample peaked at 34 dynes/cm. Cooling rates faster than the 0.15 degrees/minute shown in Fig. 3 resulted in truncated peaks below 30.5 dynes/cm.

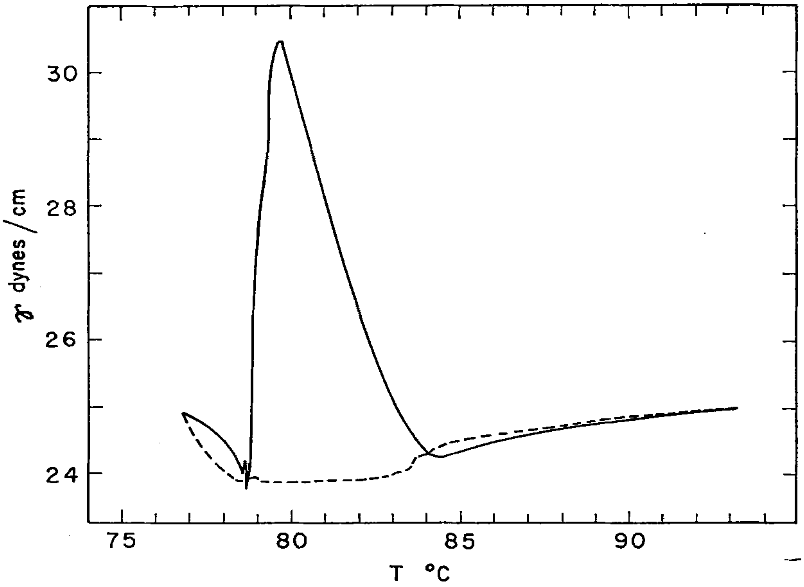

Figure 3. Surface tension of cholesteryl myristate. Solid line, cooling; dashed line, heating. Cooling rate: – 0.15 degrees/min.

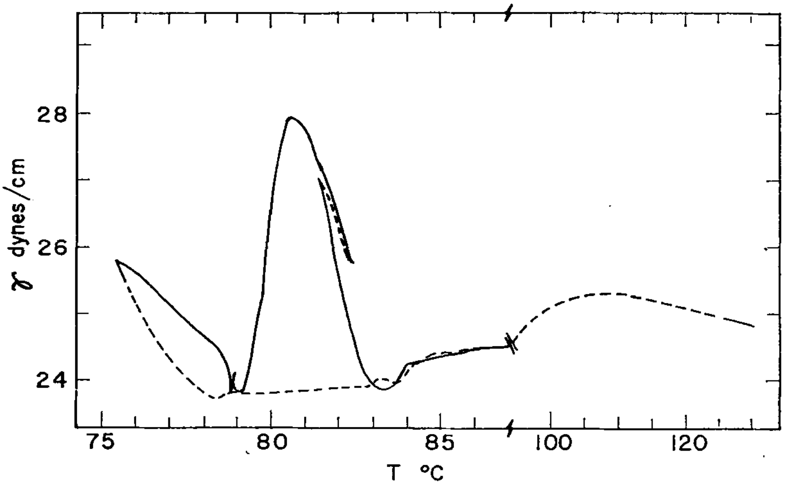

Figure 4. Surface tension of cholesteryl myristate. Solid line, cooling; dashed line, heating. Cooling rate: – 0.05 degrees min. The appendage on the cooling curve is due to a brief heating/cycle.

The lower peak height observed for the slower cooling rate (Fig. 4) suggests that the increase was due to non equilibrium thermal conditions and that the surface tension would drop to the value recorded in the heating cycle if the sample were brought to thermal equilibrium. However, when a run was made in which the sample was cooled to 82° and then held at that temperature for two hours, the surface tension remained constant at 25.5 ± 0.1 dynes/cm.

Figure 4 also shows the results of an attempt to establish the thermal reversibility of the major surface tension anomaly. During this run the cooling was interrupted in the region of increasing surface tension and the sample was heated slightly before cooling was resumed. This cycle which took 65 minutes is shown by the appendage originating at 81.5°. In another run the cooling was interrupted at the surface tension peak. In a period of 40 minutes the surface tension fell to the value observed for the cholesteric phase in the heating mode. At the present time it is not known whether this drop in surface tension is due to reorientation of the surface or dewetting of the slide.

The surface tension of the cholesteric phase in the heating mode showed little temperature dependence. In most runs a small anomaly of about 0.05 dynes/cm appeared one-half degree below the cholesteric-isotropic transition. This may be related to a shoulder on DTA and Polarized Light Intensity curves reported for cholesteryl myristate at this transition[7].

Measurements in the smectic phase were very erratic. All samples exhibited an initial steep rise in surface tension at the cholesteric to smectic transition followed by a sharp drop which again could be due to dewetting of the slide. On further cooling the surface tension increased but the slope was not reproducible nor was there any correlation with cooling rate. Also, large thermal hysteresis, both positive and negative, was observed.

Strip chart recordings of the electrobalance output were very smooth in the isotropic phase but became noisy at the isotropic-cholesteric transition and remained so through the cooling mode into the smectic phase. On heating, the noise subsided at the smectic-cholesteric transition. Photographs of recorder traces for the run of Fig. 4 are shown in Fig. 5. When the temperature was held constant for two hours in the high surface energy cholesteric state the noise persisted. It is evident that the surface state is highly agitated. Since this occurs in regions of high $d\gamma/dT$ it may be the result of local thermal fluctuations. The highest value observed for $d\gamma/dT$ was about 3 dynes/cm per degree. A noise level of 0.1 dynes/cm would result from a thermal variation of 0.03 degrees. Because of the mass of the stainless steel clad thermocouple, variations of this magnitude at a frequency of 5 to 10 seconds would not have been observed.

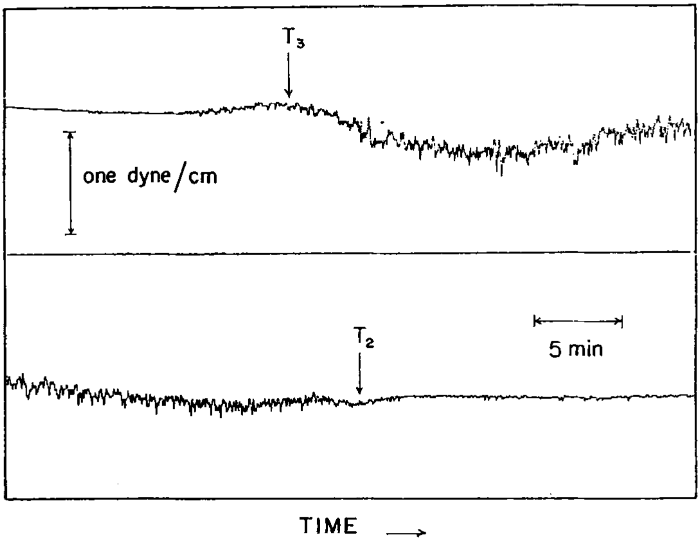

Figure 5. Photograph of recorder tracings of electrobalance signal during run shown in Fig. 4. Top curve, cooling through isotropic-cholesteric transition. Bottom curve, heating through smectic-cholesteric transition.

Although the measurements in this study were not made under isothermal conditions the surface tension of the isotropic phase and the low energy cholesteric phase was relatively independent of the thermal rate. Table 2 lists the surface tension for three samples at various thermal rates. Sample III which shows the widest deviation from the average was the only sample not recrystallized from acetone-benzene.

TABLE 2 Surface Tension of Cholesteryl Myristate in the Isotropic and Low Energy Cholesteric States

Sample	Isotropic State 94° (cooling)		Cholesteric State 82° (heating)	
	dT/dt deg/min	γ	dT/dt deg/min	γ
Ia	- 0.1	24.95	0.08	23.9
Ib	- 0.3	25.03	0.2	23.9
Ic	- 0.6	25.00	0.8	23.95
II	- 0.1	25.03		
III	- 0.12	24.80	0.14	23.5

An interesting analogy exists between these studies and viscosity-temperature curves for cholesteric esters. Ostwald[10] and Vorlander[11] have described viscosity anomalies at the isotropic-cholesteric transition with " indefinitely " high viscosities. Vorlander also noted that the anomaly was less apparent if the transition temperature was approached by heating rather than cooling.

REFERENCES

1. Green, H. S., " Handbuch der Physik ", vol. X, " Strucktur der Flüssigkeiten ", pp. 80–81, Springer Verlag, Berlin, 1960.
2. Drost-Hansen, W., *Industr. Engrg Chem.* **57**, No. 4, 18 (1965).
3. Schwartz, W. A. and Moseley, H. W., *J. Phys. and Colloid Chem.* **51**, 826 (1947).
4. Padday, J. F. and Russell, D. R., *J. Colloid Sci.* **15**, 503 (1960).
5. Porter, R. S. and Johnson, J. F., *J. Appl. Phys.* **34**, 55 (1963).
6. Barrall, E. M., Porter, R. S. and Johnson, J. F., *J. Phys. Chem.* **71**, 895 (1967).
7. Barrall, E. M., Porter, R. S. and Johnson, J. F., *Mol. Cryst.* **3**, 103 (1967).
8. Barrall, E. M., Porter, R. S. and Johnson, J. F., *J. Phys. Chem.* **70**, 385 (1966).
9. Gray, G. W., *J. Chem. Soc.*, 3733 (1956).
10. Ostwald, W. and Malss, H., *Kolloid z.* **63**, 192 (1933).
11. Vorlander, D., *Z. Krist.* **79**, 61 (1931).