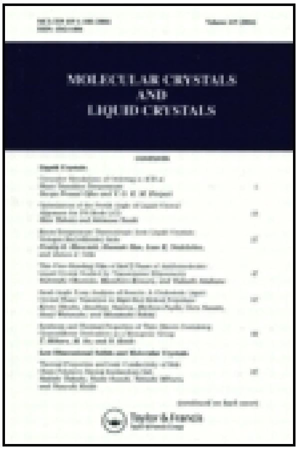

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

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Version of record first published: 19 Oct 2010.

To cite this article: D. Demus, H. G. Hahn & F. Kuschel (1978): Density Measurements in cholesteryl Myristate, Molecular Crystals and Liquid Crystals, 44:1-2, 61-70

To link to this article: http://dx.doi.org/10.1080/00268947808084968

Mol. Cryst. Liq. Cryst., 1978, Vol. 44, pp. 61–70
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Printed in Holland

Density Measurements in Cholesteryl Myristate

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(*Received January 18, 1977; in final form May 20, 1977*)

The densities of cholesteryl myristate were measured in the smectic, cholesteric, blue and isotropic phase. At the transitions smectic/cholesteric and blue/isotropic within the temperature interval of 0.01 to 0.02°K discontinuities in the density curves occured, which indicate phase transitions of first order. At the transition cholesteric/blue only a change in the expansion coefficients was observed, which points to a phase transition of second order.

Die Dichten von Cholesterylmyristinat wurden in der smektischen, cholesterinischen, blauen und isotropen Phase gemessen. An den Umwandlungen smektisch/cholesterinisch und blau/isotrop treten innerhalb eines Temperaturintervalls von 0,01 bis 0,02°K Diskontinuitäten in den Dichtekurven auf, welche Phasenumwandlungen 1. Ordnung anzeigen. An der Umwandlung cholesterinisch/blau ist nur eine Änderung in den Ausdehnungskoeffizienten vorhanden, welche auf eine Phasenumwandlung 2. Ordnung hinweist.

1 INTRODUCTION

According to different theories, in the temperature region of phase transitions of liquid crystals anomalies in the thermodynamic properties are to be expected.[1,2,3] Price and Wendorff observed such anomalies in the densities of cholesteryl myristate[4] and other cholesteryl esters,[5] but only on the low temperature side of the transition regions. Above the transitions no anomalies were found. The whole temperature intervals in which the transitions smectic/cholesteric resp. cholesteric/isotrop occured, had a breadth of 0.2 to 0.5°C. The existence of the "blue" phase[6,7] at the cholesteric substance did not show any influence on the density/temperature curves.

We reinvestigated the temperature dependence of the density of cholesteryl myristate in order to prove the unexpected absence of post transition effects and the finite breadth of the transition region. We found some differences to the results of Price and Wendorff with respect to these points of view. Additionally we could clearly show anomalies at the transition cholesteric/blue phase.

2 APPARATUS

For the density measurements we used a capillary dilatometer with a diameter of about 0.15 mm. The capillary was bent in U shape and enlarged to a bulb in its middle part. The bulb contained about 98% of the whole substance, usually about 50 mg. A thermostating arrangement was used which permitted temperature control to 0.01°C or better. Under favourable circumstances a temperature control of better than 0.005°C was reached. The substance volume was evaluated by observing the meniscus in the capillary with a cathetometer.

The main error of our method is caused by the weighing process. The absolute error of the densities is $\Delta\rho = \pm 0.0013\ \mathrm{g \cdot cm^{-3}}$. The relative error within one series with the same sample is caused mainly by the meniscus observation error and the temperature oscillations; it can be estimated to $\Delta\rho_{\mathrm{rel}} = \pm 0.00001\ \mathrm{g \cdot cm^{-3}}$. It is important that this relative error is very low. By this fact it is possible to investigate the phase transitions very carefully within one series. Larger errors of the order of magnitude of the absolute errors would not allow to detect small anomalies in the densities.

3 SUBSTANCE

We used samples of cholesteryl myristate synthesized in our laboratory. The substance was purified by ten recrystallizations from acetone to constant transition temperatures. By calorimetric analysis the substance showed impurities in an amount of 0.6 mole %.

4 RESULTS

Figure 1 shows the density of cholesteryl myristate in its liquid crystalline phases and in the isotropic state. At the transitions smectic A/cholesteric and blue phase/isotropic we found jumps in the density (see Table III), at the transition cholesteric/blue phase only a change in the slope of the nearly linear curves. This behaviour allowed the evaluation of the transition temperatures, which we compare in Table I with the results of others. Our own values show good agreement with the calorimetric and refractometric results, considering the fact that in the calorimeter the transition cholesteric/blue phase was not detected. The difference between the microscopic clearing points of cholesteryl esters and the higher calorimetric, refractometric and dilatometric ones is obviously due to the fact that by ordinary microscopy the blue phase is not observable and therefore the true clearing point cannot be detected. Price and Wendorff[4] give lower transition temperatures, which point to

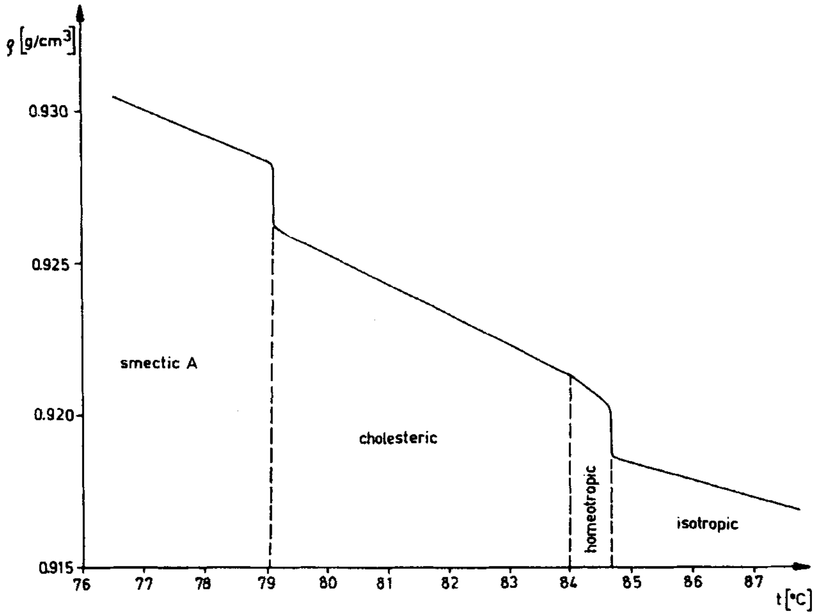

FIGURE 1 Temperature dependence of the densities of cholesteryl myristate in the different phases.

lower substance purity (which will be discussed also later) or to thermometer differences.

Semenchenko, *et al.*,[15] measured the pressure dependence of the transition temperatures. Their density values extrapolated to pressure zero lie remarkably higher than our results. The densities given by Price and Wendorff[4] agree with our absolute values within the limits of error. But remarkable differences occur in the observed temperature dependence of the density. Table II summarizes the expansion coefficients α of the two works. We found a slight temperature dependence of α within all phases, whereas Price and

TABLE I

Transition temperatures of cholesteryl myristate [°C]

Method	solid/ smectic	smectic A/ cholesteric	cholesteric/ blue phase	blue phase/ isotropic	Reference
dilatometric	—	79.16	84.05	84.64	this work
dilatometric	70.5	78.6	—	83.8	Price, *et al.*[4]
calorimetric	71.09	79.15	—	84.63	Arnold, *et al.*[8]
refractometric	—	78.8	84.0	84.5	Pelzl[11]
microscopic	71.4	79.3	84.1[a]	—	Demus, *et al.*[10]

[a] In the original work considered as clearing point.

TABLE II

Expansion coefficients

		$\alpha \cdot 10^4$ [°K^{-1}]	
Phase	Temperature region [°C]	This work[a]	Price, Wendorff[4]
smectic A	71.5–76.5	8.85	—
	76.5–77.0	9.9	—
	77.0–77.5	10.7	—
	77.5–78.0	11.2	—
	78.0–79.0	11.3	—
	70.5–78.1		7.04
cholesteric	79.3–80	12.6	—
	80 –81	11.8	—
	81 –83	11.9	—
	83 –84.0	13.5	—
	78.6–83.4	—	11.2
blue phase	84.0–84.4	18.6	—
isotropic	84.7–85	13.5	—
	85 –86	9.5	—
	>83.8	—	7.99

[a] Mean values of several investigations.

Wendorff gave constant values. Below the phase transitions smectic/cholesteric and cholesteric/isotropic Price and Wendorff found remarkable pre-transition effects in an interval of about 0.5°C, however any post-transition effect was lacking. Figure 2a and 4 (curve a) show the results of our reinvestigation. As the curves indicate, the real transition intervals are not larger than 0.01°C for the smectic/cholesteric and 0.02°C for the blue phase/isotropic transition. Within these intervals slight pre- and post-transition effects can occur and jumps in the curves can be strongly suggested, indicating phase transitions of first order. We repeated these measurements with a lower temperature constancy. As to be seen in Figure 2b, the transition interval seems to be much broader and stronger pre- and post-transition effects seem to occur. The same effect occured at the transition blue phase/isotropic phase. Measurements with substances of lower purity yielded also broader transition intervals and above a certain amount of impurities no exact transition temperatures could be detected.

Therefore we conclude that the sharpness of the transitions strongly depends on the temperature constancy within the single measurements and on the substance purity. Our own results show, that in cholesteryl myristate the typical transition phenomena are restricted to a temperature interval of

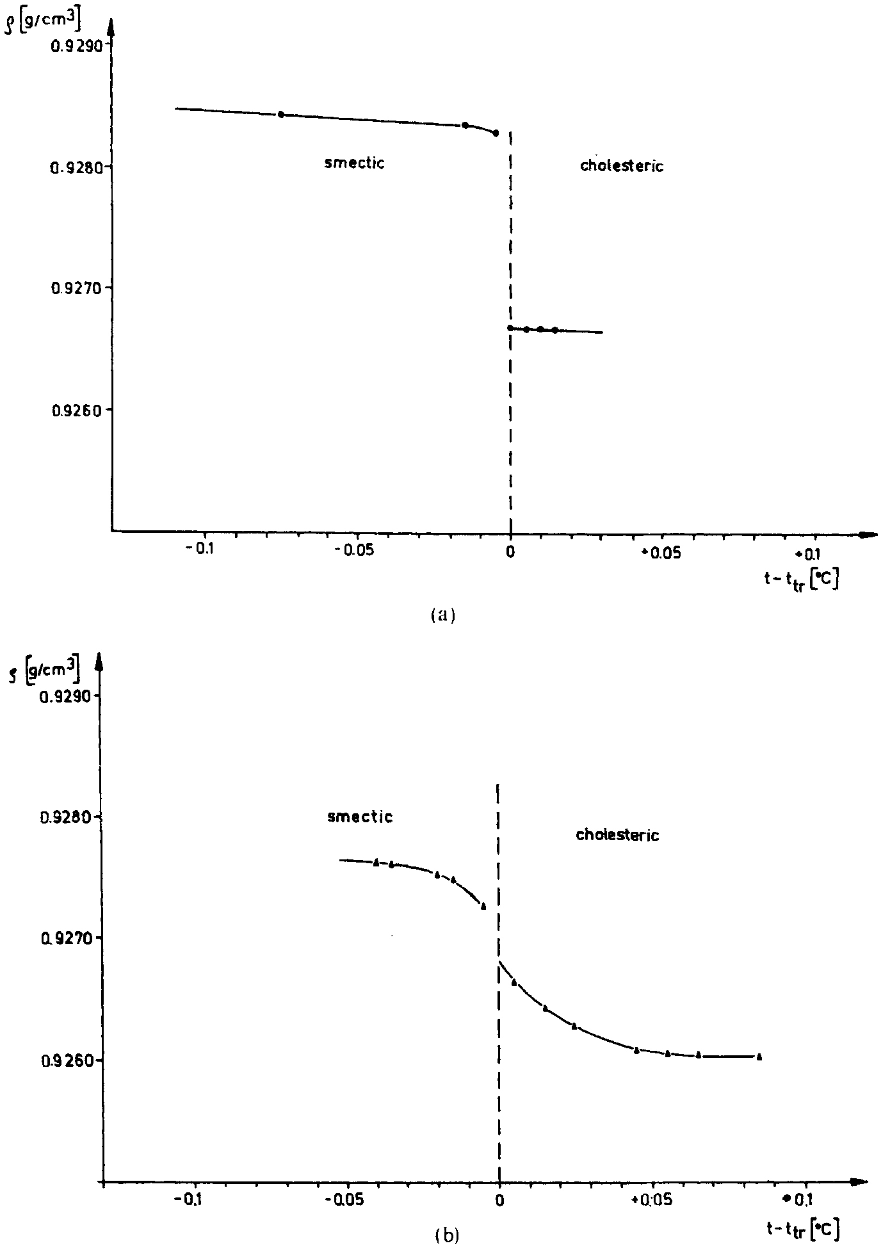

FIGURE 2 Density at the phase transition smectic A/cholesteric of cholesteryl myristate (t_{tr} = phase transition temperature).

a) Temperature constancy ≤0.01°K.

b) Temperature constancy ca. 0.02°K.

not more than 0.02°C, but the accuracy of our method does not allow to decide if this transition interval is possibly still smaller.

At the transition blue phase/isotropic we observed a hysteresis effect. With decreasing temperature we always found a broader transition interval than with increasing temperature (see Figure 4 curve b). This behaviour is also reported by Torza and Cladis[12] at the clearing point of the nematic phase of *N*-[4-cyanobenzylidene]- 4-*n*-octylaniline.

The existence region of the blue phase was of special interest in our density measurements. Figure 3 displays the interval around the transition cholesteric/blue. We repeated the investigations several times and never were we able to detect a jump in the curve. But accurately at the transition point 84.0°C we found a change in the slope of the curve which is strictly linear on both sides of the transition. The mean values of the expansion coefficients are $\alpha_{ch} = 12.8 \cdot 10^{-4}\,°K^{-1}$ for the cholesteric and $\alpha_{bl} = 18.8 \cdot 10^{-4}\,°K^{-1}$ for the blue phase. This behaviour strongly points to a phase transition of second order. Measurements with increasing temperature showed that this transition temperature always was reproducible. At decreasing temperature the behaviour depended on the velocity of cooling: with larger cooling rates the transition could be remarkably supercooled, whereas with sufficiently slow cooling rates the transition temperature coincided with that found at increasing temperature measurement. Price and Wendorff[4] could not detect

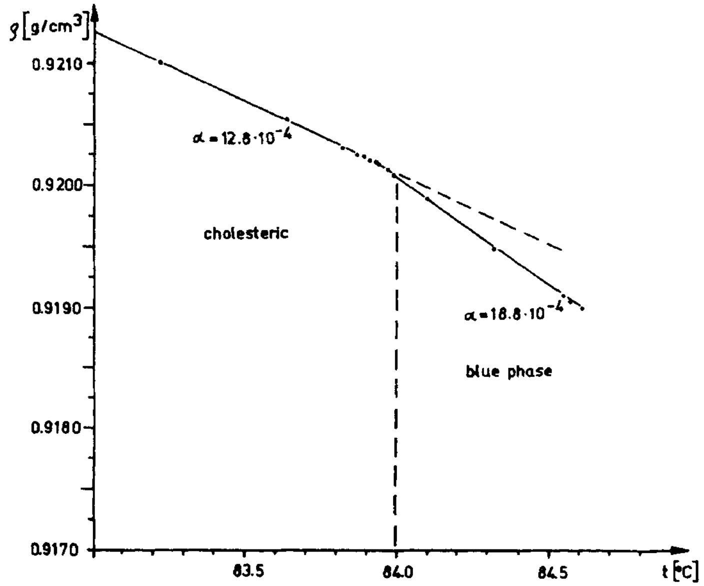

FIGURE 3 Density at the transition cholesteric/blue of cholesteryl myristate.

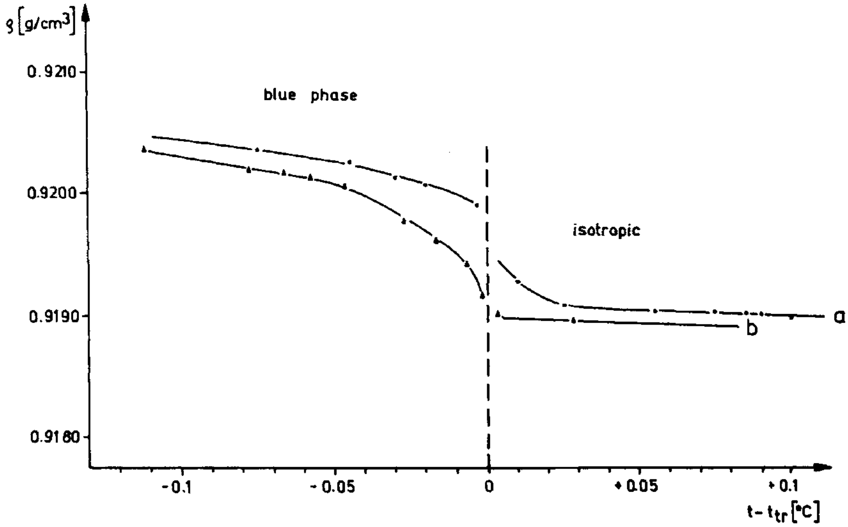

FIGURE 4 Density at the transition blue/isotropic of cholesteryl myristate (t_{tr} = transition temperature).

a) Decreasing (·) temperature.

b) Increasing (▲) temperature.

this transition in their density investigation. As the lower transition temperatures and the much broader transition intervals indicate the purity of their substance was not sufficient possibly due to the long times of up to one week, which the substances were heated during the measurements. Therefore the whole temperature region of the blue phase obviously was overlapped by the anomalies connected with the clearing process. In substances of low purity we also found curves of this kind.

In Table III the density changes at the transitions are given. We evaluated the $\Delta\rho$ by the difference of the densities at the end of the linear parts of the curve below and above the transitions. $\Delta\rho$ yielded higher values in the series with decreasing temperature. The somewhat higher $\Delta\rho$ of Price and Wendorff[4] also were measured at decreasing temperature.

Comparing the transition anomalies in our density measurements with the calorimetric investigations of Arnold and Roediger[8] it is obvious, that the transition intervals derived from the density resp. expansion coefficient curves are much smaller (ca. 0.01–0.02°C) than those obtained from the temperature dependence of the heat capacity (several degrees). It is to be expected that this behaviour is not restricted to cholesteryl myristate, but is a general phenomenon. The volumes V resp. densities ρ are connected

TABLE III

Change of the density at the transitions

Transition	$\Delta\rho[\mathrm{g\cdot cm^{-3}}]$	Reference
smectic A/cholesteric	0.0016[a]	Price, *et al.*[4]
	0.00154[b]	this work
	0.00168[c]	this work
cholesteric/isotropic	0.0016[a]	Price, *et al.*[4]
blue/isotropic	0.00128[b]	this work
	0.00138[c]	this work

[a] Taken from graph in Ref. 4; in Table II of Ref. 4 is given: $\Delta V_{s/ch} = 0.14\%$, $\Delta V_{ch/i} = 0.17\%$.

[b] Mean value from measurements with increasing temperature.

[c] Mean value from measurements with decreasing temperature.

with the Energy E of a substance by well known equations of the Lennard-Jones type:[16]

$$E = \frac{-A}{V^2} + \frac{B}{V^4} = -A'\rho^2 + B'\rho^4$$

(A, A', B, B' are constants).

According to the higher power of the density in this equation small anomalies in ρ cause remarkable effects in the energy. The density therefore is a property which is not very sensitive to fluctuations or pre-transition phenomena, which can be estimated easier in the heat capacities,[8,9] elastic constants[14] or especially in some optical properties as for instance the selective reflection of circulary polarized light in cholesteric phases.[13]

5 OBSERVATIONS CONCERNING THE BLUE PHASE

On observation with increasing temperature, the blue phase became visible optically in the capillaries because of the scattering of blue light[6,7] which occured at the same temperature as that at which the change in slope of the density curve took place. With decreasing temperature the blue light reproducibly appeared at the clearing point. At high cooling rates the blue colour persisted to temperatures below 84.0°C. Only with slow cooling rates exactly at 84.0°C the cholesteric focal conic texture appeared. This behaviour is full consistent with the results of the density measurements.

Pelzl[11] found by refractometric investigations that the blue phase possesses only one refraction index n_b (no double refraction), which at the clearing temperature is somewhat higher than the refractive index n_i of the isotropic phase.

Using the equation of Lorenz and Lorentz

$$\frac{n^2 - 1}{n^2 + 1} \cdot \frac{M}{\rho} = \frac{4\pi}{3} N_L \alpha$$

(M = mole mass, N_L = Loschmidt's number)

and assuming the same value of the polarizability α for both phases, the jump in the refractive indices can be reduced to a jump of the densities. With Pelzl's values $n_b = 1.4800$ and $n_i = 1.4790$, taking into consideration the possible errors of the n values, we could calculate two extreme values for the corresponding density jump:

$$0.00086 < \Delta\rho < 0.00231 \ [\mathrm{g \cdot cm^{-3}}]$$

Our experimental values

$$0.00128 < \Delta\rho < 0.00168$$

as well as the results of Price and Wendorff[4] lie nearly in the middle of the calculated interval.

In the spectrophotometric investigation of the blue phase we found a minimum in the transparency for 20 μm layer thickness at 353 nm and for 100 μm layer thickness at 360 nm. The substance does not have an absorption region at these wavelengths, therefore the minimum in the transparency must be interpreted in terms of light scattering. The blue colour observed with the naked eyes is good compatible with this interpretation.

Arnold and Roediger[8,9] observed more than one peak in the calorimetric investigation of the phase transition cholesteric/isotropic of several cholesteryl esters, especially also cholesteryl myristate. A second additional peak occured several tenth of a degree below the true clearing peak. It seems reasonable to discuss this additional peak in connection with the occurence of the blue phase. But otherwise it is necessary to remember that also for the transition smectic A/cholesteric several peaks were observered.[8,9] Therefore a general interpretation of the splitting of the transition peaks in the calorimetry seems to be possible by the conception, that the molecules do not transform in one step, but there are several steps during the transition connected with the transformation of different chemical groups of the molecule. Further investigations with different methods are necessary to prove this idea. It seems very probable to us that the anomalies in the density/temperature curves connected with the occurrence of the blue phase are observable also in other substances. Therefore we are conducting further investigations in this direction.

Acknowledgement

For discussions and his help during the spectrophotometric measurements we are indebted to Dr. G. Pelzl. For valuable remarks we thank Prof. Dr. H. Sackmann.

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