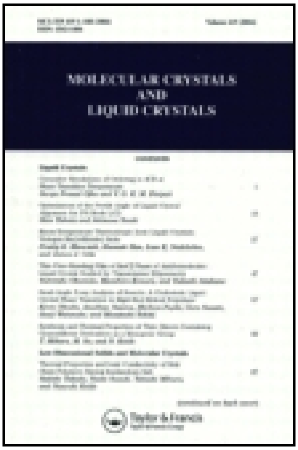

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Pressure Dependence of the Cholesteric Pitch Below and Above a Tricritical Point. Studies on Cholesteryl Myristate and Cholesteryl Oleyl Carbonate Near the Cholesteric-to-Smectic a Phase Transition

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PRESSURE DEPENDENCE OF THE CHOLESTERIC PITCH BELOW AND ABOVE A TRICRITICAL POINT. STUDIES ON CHOLESTERYL MYRISTATE AND CHOLESTERYL OLEYL CARBONATE NEAR THE CHOLESTERIC-TO-SMECTIC A PHASE TRANSITION

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Abstract: In order to study the influence of a tricritical point on the untwisting of the cholesteric helix near the phase transition cholesteric-to-smectic A light reflection measurements were carried out with cholesteryl oleyl carbonate (COC) and cholesteryl myristate (CM) up to 4.5 kbar and 95 °C. The untwisting of the helix can be observed by the divergence of the wavelength of maximum light reflection λ_R with pressure in the phase transition region.

Whereas the existence of a tricritical point in the phase diagram of COC is already known experimental evidence could be given in the case of CM as well.

A comparison of the pressure dependence of λ_R for COC as well as for CM below and above the tricritical point shows that the divergence of λ_R with pressure is only little altered by the change in phase transition order.

Introduction: The transformation of a cholesteric to a smectic mesophase by pressure or temperature variation can sensitively be studied by light reflection measurements. The wavelength of maximum light reflection λ_R is proportional to the pitch z of the cholesteric helix according to

$$\lambda_R = \bar{n} \cdot z \qquad (1)$$

where $\bar{n}$ denotes the average refractive index of the phase.[1] Since the phase transition is accompanied by an untwisting of the helix a divergence of $\lambda_R(p,T)$ is observed.[2]

The transitions cholesteric-smectic A of pure substances at atmospheric pressure known so far are first order, that is a change in volume and enthalpy occurs. Keyes et al.[3] and Shashidhar et al.[4] however have shown for cholesteryl oleyl carbonate (COC) that the application of high pressures can change a phase transition cholesteric-smectic A from first to higher order. The point in the pressure-temperature phase diagram corresponding to this change of order is called a tricritical point.

In the case of COC we have already shown that a tricritical point is detected also in a phase diagram based upon light reflection measurements.[5] The tricritical point appears as an intersection of two straight lines which represent first order behavior below and higher order one above this singular point (Figure 1).

The transition cholesteric-to-smectic which is often associated with pretransition phenomena occurs within a finite pressure or temperature region. As has been found by volume measurements[6,7] cholesteryl myristate (CM) reveals an unusually narrow transition region, whereas that of cholesteryl oleyl carbonate (COC) is essentially more extended. This behavior can be seen also from Figures 2 or 3 where near a phase transition cholesteric-to-smectic A the pressure dependence of λ_R at constant temperature for CM and COC is shown.* The narrow transition region of CM exhibits itself in the very rapid divergence of $\lambda_R(p)$. The motivation for our experiments was to investigate, of the divergence of $\lambda_R(p)$ especially that very rapid one of CM is essentially influenced by the existence of a tricritical point.

First of all, the existence of a tricritical point for CM must be proved experimentally since Semenchenko et al.[9] have only predicted that the change in the effective volume during the cholesteric-smectic A phase transition determined by them up to 0.800 kbar would approach zero at about 1.050 kbar and 107°C. In order to get a phase diagram of CM we have measured 20 isotherms, two of which have already been shown in Figures 2 and 3 respectively. Phase transition pressure p_u is that pressure where λ_R approaches infinity.[5] The resulting transition pressures p_u were plotted *vs* the

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*For the experimental technique employed in this investigation see reference 8.

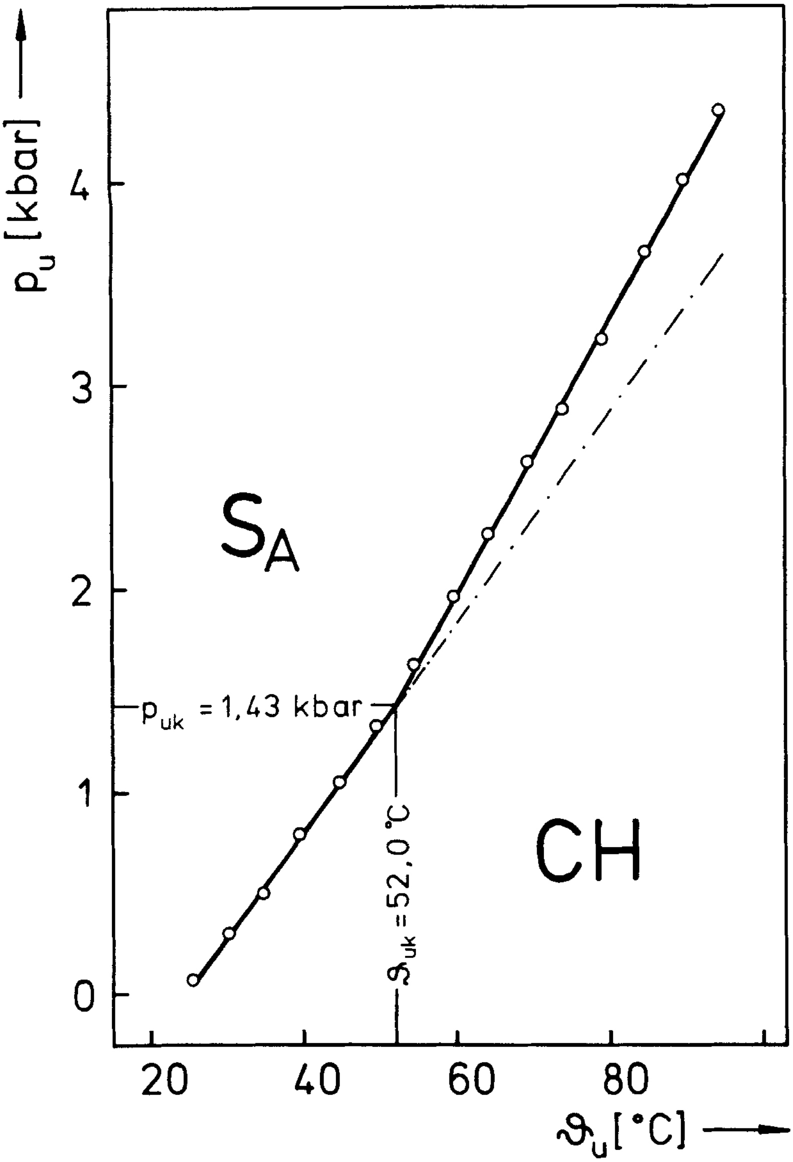

Figure 1: The p_u-θ_u phase diagram of cholesteryl oleyl carbonate (CH = cholesteric, S_A = smectic A; p_{uk}, θ_{uk}: coordinates of the tricritical point)

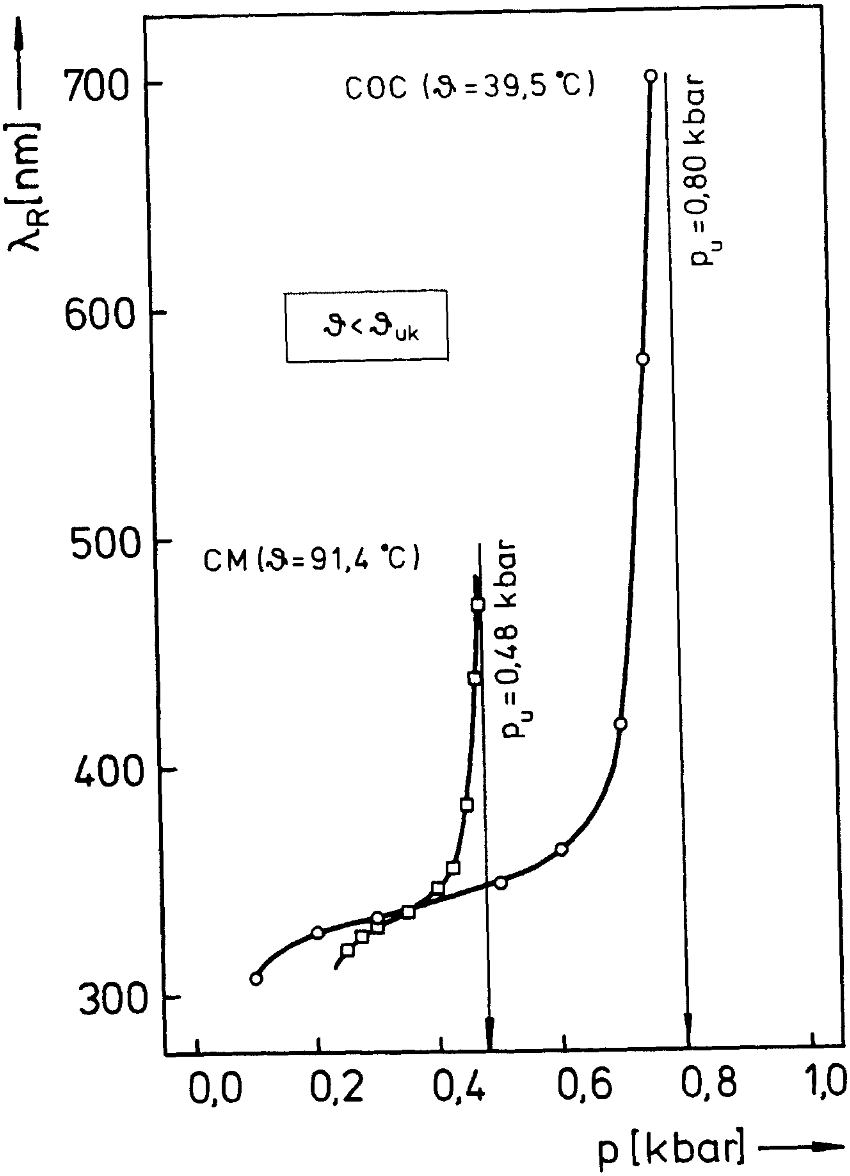

Figure 2: Pressure dependence of the wavelength of maximum light reflection λ_R for cholesteryl oleyl carbonate (COC) and cholesteryl myristate (CM) at a temperature θ below θ_{uk} of the tricritical point (p_u = phase transition pressure)

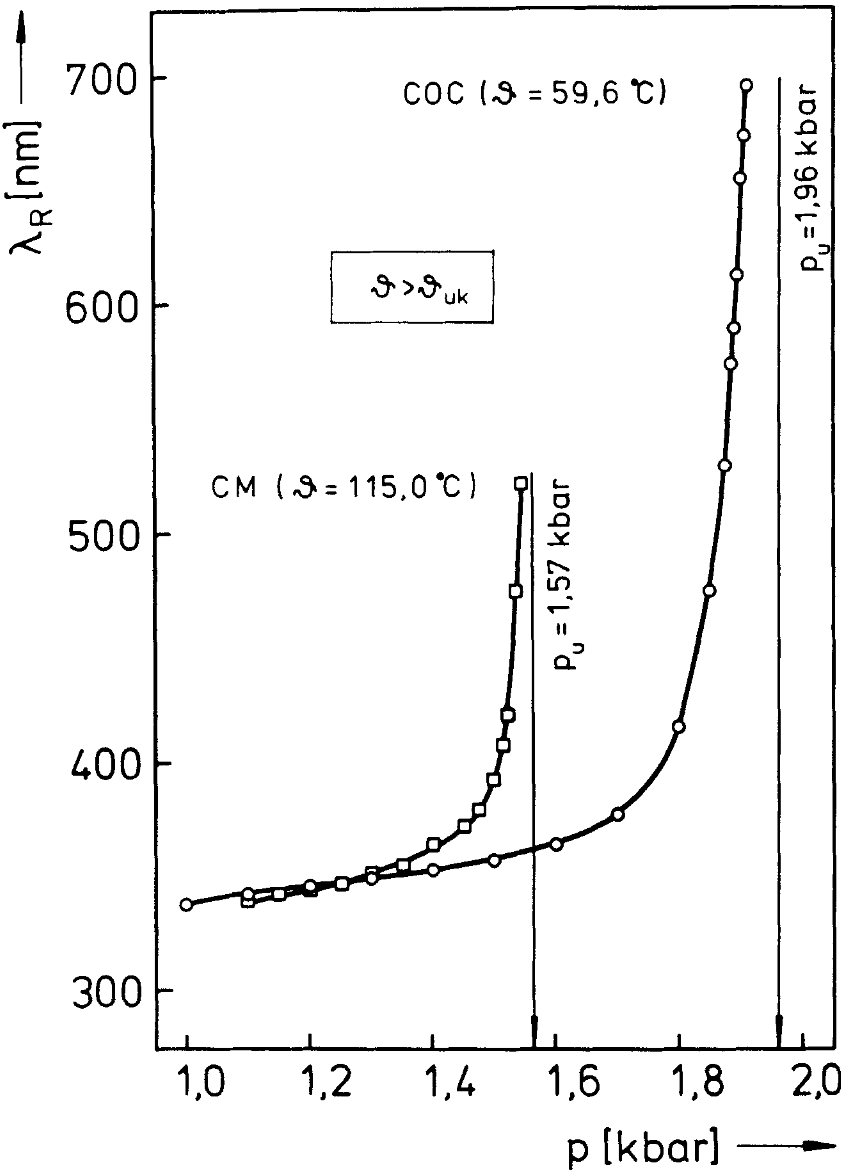

Figure 3: Pressure dependence of the wavelength of maximum light reflection λ_R for cholesteryl oleyl carbonare (COC) and cholesteryl myristate (CM) at a temperature θ above θ_{uk} of the tricritical point (p_u = phase transition pressure)

transition temperatures θ_u in Figure 4. The plot gives two straight lines which intersect at p_{uk} = 1.051 kbar and θ_{uk} = 105.1°C. These intersection coordinates are in excellent agreement with those having been obtained by extrapolation according to Semenchenko (Table I) and thus give evidence for a tricritical point of CM.

Table I: Pressure-temperature coordinates p_{uk} - θ_{uk} of the tricritical point of cholesteryl myristate

	p_{uk} [kbar]	θ_{uk} [°C]
Semenchenko et al.[9]	1.050	107
This work	1.051	105.1

To test furthermore the phase diagrams for CM and COC in Figures 1 and 4 we have applied the Clausius Clapeyron equation to the function p_u (θ_u) below the tricritical point and thus calculated the transition enthalpies at atmospheric pressure by means of the known corresponding changes in volume. These enthalpy values were compared with those obtained directly by differential scanning calorimetry (Table II).[1] The corresponding values agree within the measuring accuracy.

Table II: Changes in volume ΔV and enthalpy ΔH for the cholesteric-smectic A transitions of cholesteryl oleyl carbonate (COC) and cholesteryl myristate (CM)

	ΔV [$cm^3 mol^{-1}$]	ΔH [$calmol^{-1}$] calculated	ΔH [$calmol^{-1}$] measured
COC	0.411 (ref. 7)	150 ± 10	150 ± 10 (ref. 10)
CM	1.015 (ref. 9)	355 ± 15	360 ± 15 (ref. 10)

The pressure dependences of the pitch z ($\sim\lambda_R$) at constant temperature below and above the tricritical point shall now be compared with one another and that near the cholesteric-to-

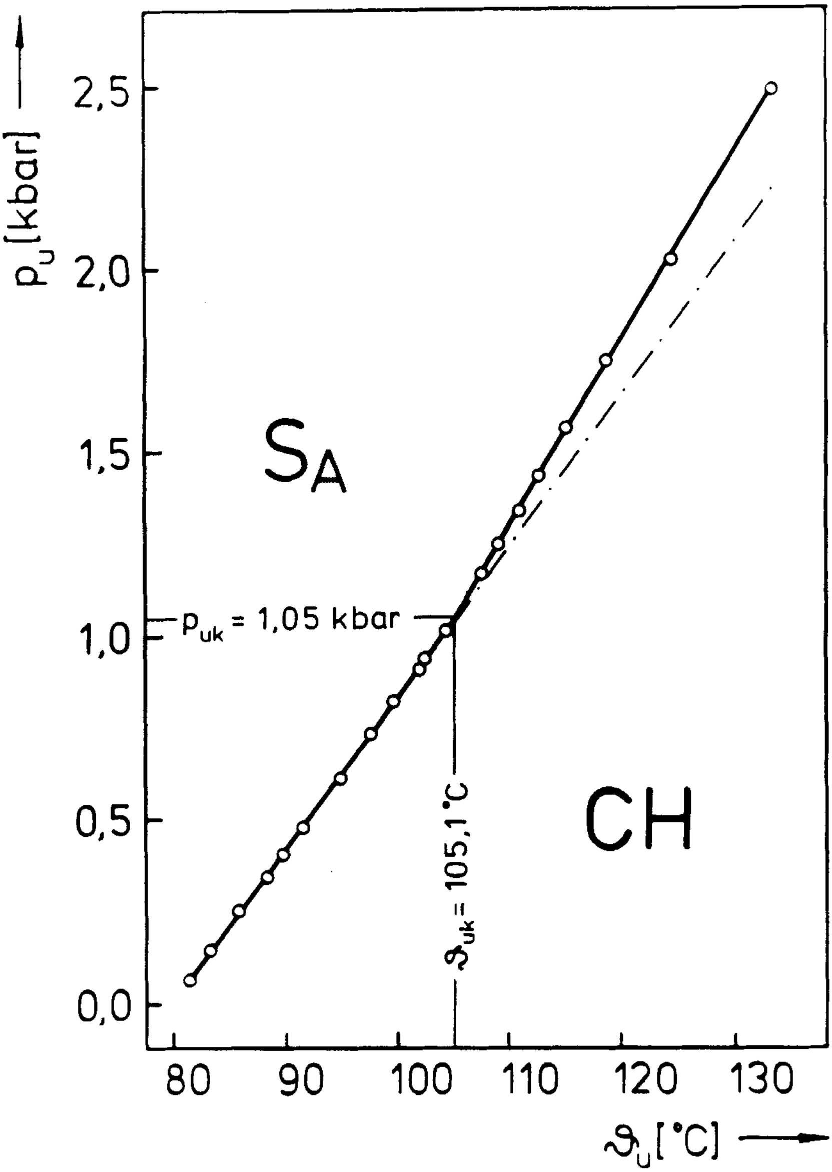

Figure 4: The p_u-θ_u phase diagram of cholesteryl myristate (CH = cholesteric, S_A = smectic A; p_{uk}, θ_{uk}: coordinates of the tricritical point)

smectic A phase transition. The pressure dependence of λ_R (z) of CM and COC respectively at a temperature in some distance below the tricritical point is displayed in Figure 2 that in some distance above this point in Figure 3. Evidently the divergence of both λ_R(p)-curves is little altered by the change in the phase transition order. The curves diverge only somewhat slower. Although the phase transition has changed from first to higher order, the untwisting of the helix of CM caused by the phase transition still occurs in a very narrow region.

Finally, the advantage of the light reflection measurements carried out in this work should be pointed out. Whereas in most cases observation of the transition region cholesteric-to-smectic by means of volume measurements is possible only as far as the transition is first order--the "discontinuity region" in the volume--temperature (-pressure) curve diminishes to a break at the tricritical point--light reflection measurements allow observation above the tricritical point as well.

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