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A PRESSURE INDUCED REENTRANT CHOLESTERIC PHASE IN A TERNARY
SYSTEM OF CHOLESTERYL N-ALKANOATES
LIGHT REFLECTION MEASUREMENTS IN MIXTURES OF CHOLESTERYL
PROPIONATE, -NONANOATE AND -TETRADECANOATE UP TO 3000 BARS

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Abstract: A pressure induced reentrant behaviour of a nematic liquid crystal was first shown by Cladis¹. For cholesteric liquid crystals such behaviour could be observed only at atmospheric pressure^{3,4,5,6}. With one exception⁷ (reentrant nematic at atmospheric pressure) all systems investigated until now - nematics as well as cholesterics - have at least one compound with a terminal-polar group.

In the light reflection measurements up to 3000 bars in a ternary mixture of cholesteryl propionate, -nonanoate and -tetradecanoate reported here, we show that liquid crystals without polar end groups can show a pressure induced reentrant behaviour as well.

Introduction In 1975 Cladis¹ observed the sequence of phases nematic, smectic, nematic by decreasing the temperature from the nematic phase of a mixture of two liquid crystals. The nematic phase at lower temperatures was called a "reentrant" nematic. Some time later Cladis et al.² found the same phenomenon for pure compounds under pressure. Starting from the nematic phase at atmospheric pressure the pure compound passed through the same sequence of phases mentioned above with isothermally increasing pressure. With one exception⁷ (reentrant nematic at atmospheric pressure) all systems investigated until now have at least one compound with a terminal-polar group which mostly is a cyano-group. The same is the case for cholesteric liquid crystals (investigations at atmospheric pressure: mixtures^{3,4,5}, pure compound⁶). According to Cladis¹ the cyano-group causes an association of the molecules in antiparallel pairs. In the case of the pressure induced nematic reentrant phenomenon, this results at higher pressures in a buckling destabilization of the smectic layers and finally in a reentrant nematic phase with a denser packing of the pairs.

In the following we show that in cholesteric liquid crystal mixtures without any compound with a cyano-group, a pressure in-

duced reentrant cholesteric phase can occur, too.

Results and discussion In the course of several investigations of the light reflection of cholesteric liquid crystal mixtures we observed an unusual pressure behaviour of λ_R , the wavelength of maximum light reflection. It has been known for a long time that pure cholesteryl n-alkanoates and mixtures of them can show a divergence of λ_R when approaching the phase transition cholesteric (CH)/smectic A (S_A) at constant pressure and decreasing temperature or at constant temperature and increasing pressure. Therefore we were very surprised when λ_R of a ternary mixture of cholesteryl propionate (CP), -nonanoate (CN) and -tetradecanoate (CT) (see 52.94°C - isotherm in fig. 1; molar fraction $X_{CP} = 0.150$), after an expected increase with pressure,

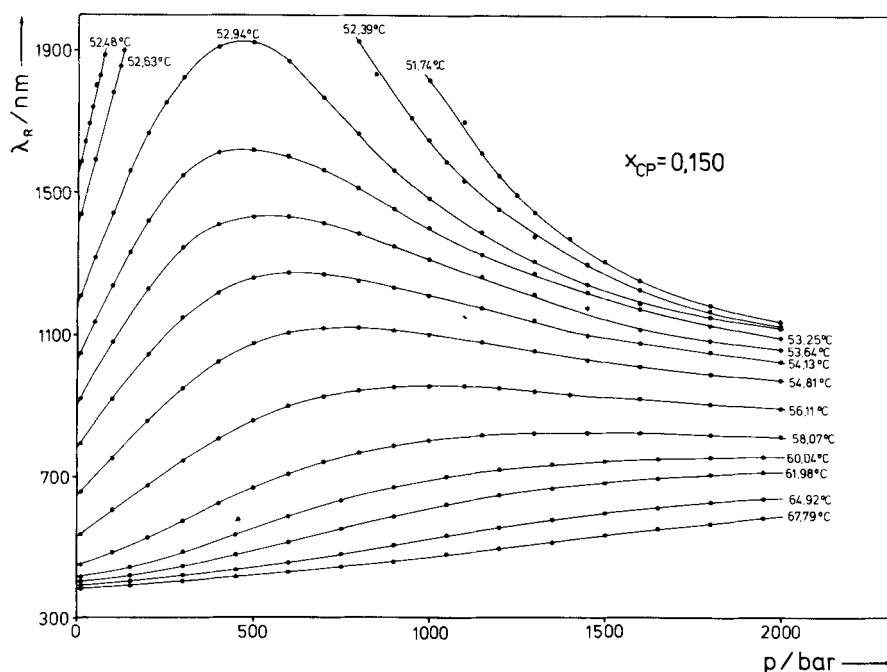


FIGURE 1 Pressure (p) dependence of the wavelength of maximum light reflection λ_R at various temperatures for a ternary mixture of cholesteryl propionate (CP), -nonanoate (CN) and -tetradecanoate (CT) (ratio of molar fraction:
 $X_{CP} : X_{CN} : X_{CT} = 0.150 : 0.577 : 0.273$;
 $X_{CN} : X_{CT} = 2.11 : 1.00$)

finally decreased with further pressurizing. Because all components of the mixture form a left-handed helix, a compensation effect cannot explain this behaviour. To the best of our knowledge, a reentrant behaviour of the cholesteric phase is probably the reason for this unusual pressure dependence of λ_R . For further examination of this question, we measured some additional isotherms of the mixture with $X_{CP} = 0.150$ (see fig. 1) and extended our investigations to a second mixture with $X_{CP} = 0.120$ ($X_{CN} : X_{CT} = 2.11 : 1.00$ for both mixtures) (see fig. 2).

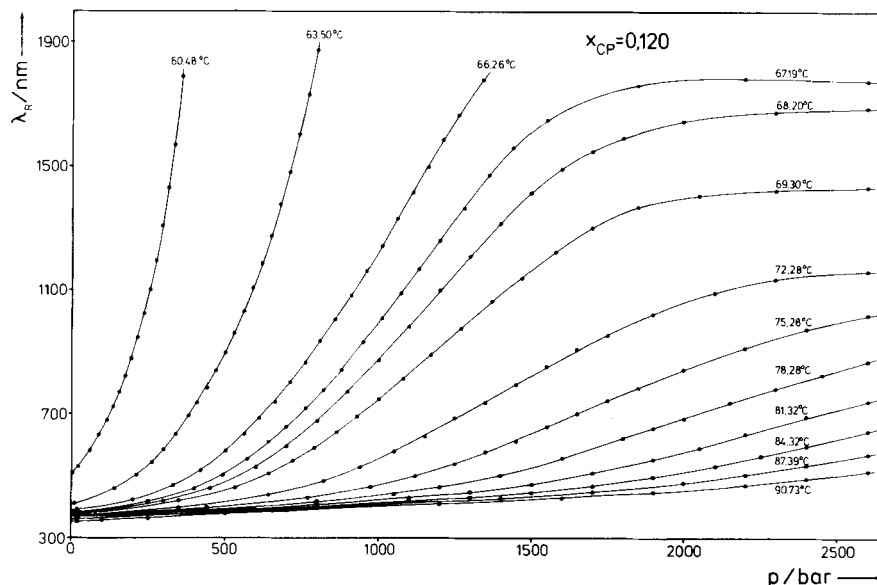


FIGURE 2 Pressure (p) dependence of the wavelength of maximum light reflection λ_R at various temperatures for a ternary mixture of cholesteryl propionate (CP), -nonanoate (CN) and -tetradecanoate (CT) (ratio of molar fraction:

$$X_{CP} : X_{CN} : X_{CT} = 0.120 : 0.597 : 0.283 ;$$

$$X_{CN} : X_{CT} = 2.11 : 1.00)$$

For determining the phase transition point CH/S_A from the pressure (p) dependence of λ_R at constant temperature, either a breakoff or a strong divergence of the λ_R -isotherm with p must be observable. In the majority of isotherms (see fig. 1 and 2) this is not the case so that we were forced to convert the pressure dependence into a temperature dependence of λ_R using the measured isotherms. The divergences of these λ_R -isobars were

strong enough to determine the phase transition temperature T_t according to the function

$$\lambda_R = A \cdot \left(\frac{T}{T_t} - 1 \right)^{-B} \quad (1)$$

for $\lambda_R \rightarrow \infty$.

A , B and T_t are the best fit parameters of the function. This method of determination of the phase transition point CH/S_A has been previously described by Pakusch⁸.

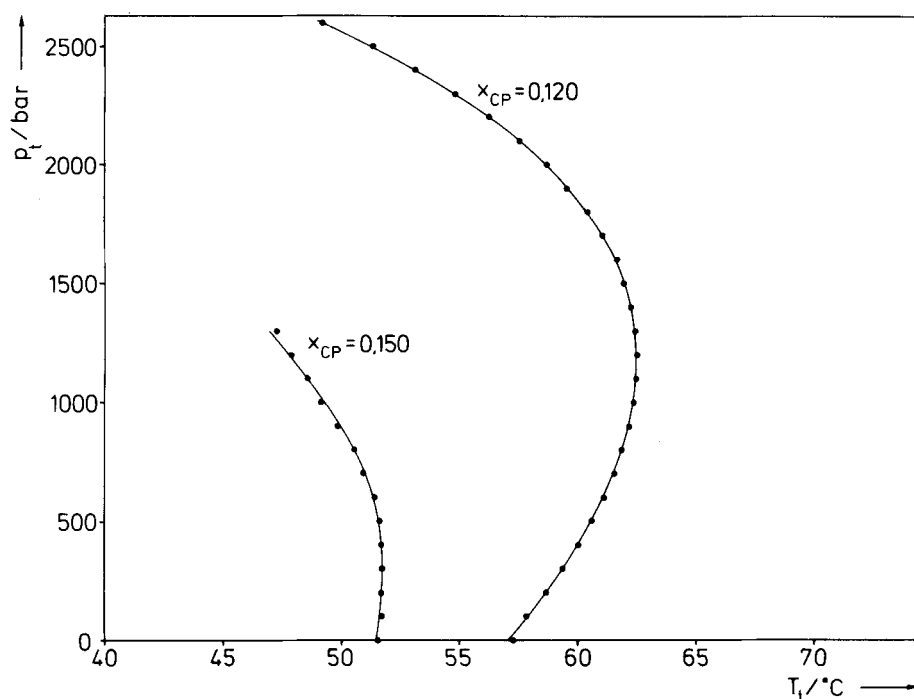


FIGURE 3 Phase transition cholesteric/smectic A: phase transition pressure p_t versus phase transition temperature T_t of two ternary mixtures of cholesteryl propionate (CP), -nonanoate (CN) and -tetradecanoate (CT); (ratio of molar fraction: $X_{CP} : X_{CN} : X_{CT} = 0.150 : 0.577 : 0.273$, $0.120 : 0.597 : 0.283$, respectively; $X_{CN} : X_{CT} = 2.11 : 1.00$)

The obtained phase equilibrium line CH/S_A of the ternary mixture with $x_{CP} = 0.120$ shows clearly the change from a positive

to a negative gradient. The smectic A phase, however, is always the low-temperature phase. Now the pressure dependence of the 52.94°C-isotherm in figure 1 is understandable: starting from the cholesteric phase at atmospheric pressure (see fig. 3), since one is approaching the smectic A phase when the pressure is raised at 52.94°C, λ_R increases; at still higher pressures, one is going away from the smectic A phase, so λ_R decreases.

Only in the case of the mixture with $X_{CP} = 0.150$ could we prove directly a phase transition $S_A \rightarrow CH$ with increasing pressure by our λ_R -measurements: starting in the smectic A phase at atmospheric pressure (microscopic observation of a smectic texture) the pressure was increased at constant temperature until a light reflection band appeared which is characteristic for a cholesteric phase. In the case of the mixture with $X_{CP} = 0.120$, this proof was not possible because λ_R of the reentrant cholesteric phase was too large (> 2000 nm) to be measured with our spectrometer.

Preliminary microscopic observations under pressure in these ternary mixtures performed by Herrmann and Schneider⁹ seem to confirm the existence of a reentrant cholesteric phase at high pressure.

CP, the component with a significantly shorter alkane chain than CN and CT, probably causes similar volume conditions as in the case of the cyano-compounds but without forming antiparallel pairs of molecules. Because the ternary system described above is of high thermodynamic interest, especially with regard to the change from a discontinuous to a continuous phase transition¹, volumetric and calorimetric measurements at atmospheric pressure as well as at elevated pressure are underway.

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