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Differential Thermal Analysis (DTA) and Differential Scanning Calorimetry (DSC): Measurements on the Tricritical Behaviour of the Smectic A/Cholesteric Phase Transition of Cholesterylmyristate

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DIFFERENTIAL THERMAL ANALYSIS (DTA) AND DIFFERENTIAL SCANNING CALORIMETRY (DSC): MEASUREMENTS ON THE TRICRITICAL BEHAVIOUR OF THE SMECTIC A/CHOLESTERIC PHASE TRANSITION OF CHOLESTERYLMYRISTATE

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Abstract The phase behaviour and the transition enthalpy of cholesterylmyristate has been studied by DTA and DSC up to 3 kbar in the temperature range 300 to 600 K. The transition enthalpy for the smectic A/ cholesteric transition was extrapolated to vanish at about 3 kbar, thus suggesting a change in the order of the transition from first to second.

Introduction In the literature some discrepancies exist about the tricritical behaviour of cholesterylmyristate. According to the McMillan theory[1] a change of transition order from first

to second should occur along the transition line smectic A/cholesteric (smA/ch).

This prediction was confirmed by Pollmann and Scherer[2] who observed a so-called tricritical point for the smA/ch transition at about 1.o5 kbar and 380 K. Shashidhar[3], however,did not find this tricritical point within the pressure range up to 1.5 kbar.

In order to clear up this situation the enthalpy change along the coexistence line smA/ch has been measured directly by differential thermal analysis (DTA) and differential scanning calorimetry (DSC).

Experimental Details of the experimental DTA equipment are described in references[4,5] and of the DSC apparatus in references.[6,7] For evaluation of the results from the experimental data, for accuracy etc also see the references given above.

Results Figure 1 shows the p-T phase diagram of cholesterylmyristate obtained by DTA. The curves were fitted by a quadratic form, $T/K = a + b\,(p/bar) + c\,(p/bar)^2$; the parameters a, b and c are given in Table 1. At normal pressure two solid (s), the smectic A, the cholesteric and the isotropic liquid (l) phases exist. At about 1250 bar and 382.5 a triple point s2/smA/ch was found. Thus the

Table I: Phase transition temperatures T of cholesterylmyristate as a function of pressure p: Coefficients of the polynomials $T/K = a+b(p/bar) + c(p/bar)^2$

	a	$b.10^3$	$c.10^6$
s_1/smA	342.9	27.2	-1.32
s_2/smA	343.o	35.9	-2.86
smA/ch	352.1	27.8	-2.34
ch/l	357.7	39.9	-2.84

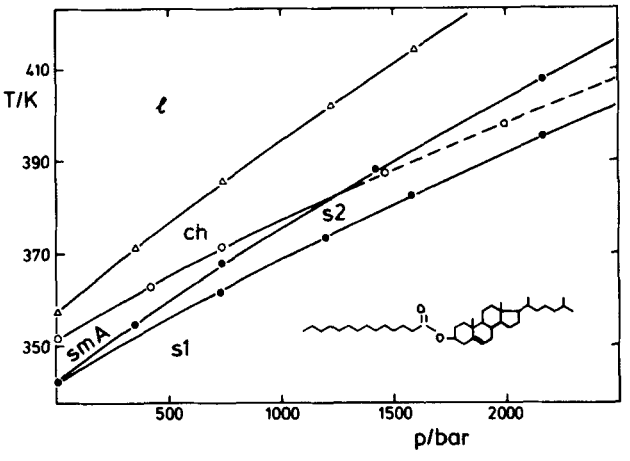

Figure 1: p-T phase diagram of cholesteryl-myristate. The hatched line corresponds to the smA/ch phase transition in the supercooled region.

smA/ch transition is monotropic at higher pressures and could only be observed in cooling runs in the supercooled region. Below 1250 bar, however, the smA/ch transition is enantiotropic.

The decrease of the enthalpy change ΔH along the coexistence line of the smA/ch transition is shown in Figure 2. The agreement between DTA and DSC measurements is good. The extrapolated curve shows that the enthalpy change will reach zero at about 3 kbar.

The same effect is demonstrated by calculating the volume change ΔV to 3 kbar (see Fig. 3). These values were obtained by using the enthalpy changes, the $(dT/dp)_{coex}$ values along the coexistence curve smA/ch and the Clausius-Clapeyron equation. In the low pressure region the data are in good agreement with those found by Semenchenko et al.[8]

Conclusions The experimental results suggest that the smA/cholesteric phase transition changes its order from first to second in the 3 kbar region. This is in accordance with the results of Shashidhar[3] that the change of order will only occur above 1.5 kbar whereas the tricritical point was found at 1.05 kbar only by Pollmann and Scherer.[2]

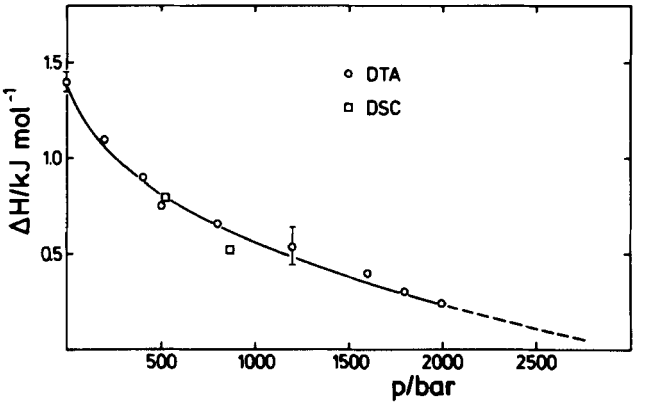

Figure 2: Enthalpy change ΔH of the smA/ch transition of cholesterylmyristate as a function of pressure p along the coexistence line.

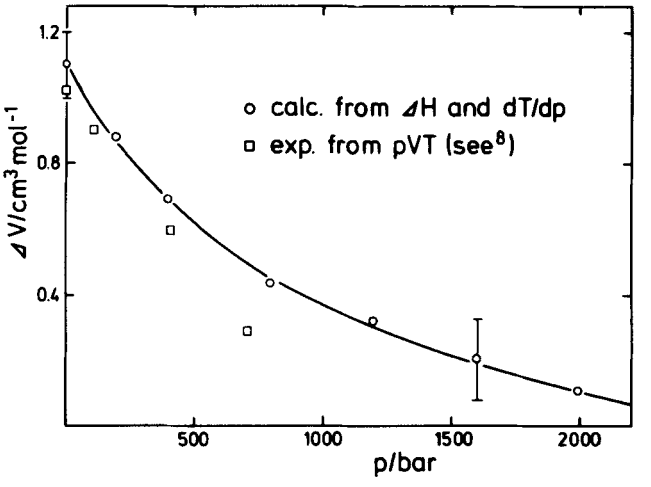

Figure 3: Volume change ΔV of the smA/ch transition of cholesterylmyristate as a function of pressure p along the coexistence line.

References

1. W.L. McMillan, Phys. Rev., A4, 1238 (1971)
2. P. Pollmann and G. Scherer, Mol. Cryst. Liq. Cryst. Lett., 34, 189 (1977)
3. R. Shashidhar, Mol. Cryst. Liq. Cryst., 43, 71 (1977)
4. A. Würflinger and G.M. Schneider, Ber. Bunsenges. Phys.Chem., 77, 121 (1973)
5. W. Spratte and G.M. Schneider, Mol. Cryst. Liq. Cryst., 51, 1o1 (1979)
6. M. Kamphausen, Rev. Sci. Instrum.,46, 668 (1975)
7. R. Sandrock, M. Kamphausen and G.M. Schneider, Mol. Cryst. Liq. Cryst., 45, 257 (1978)
8. V.K. Semenchenko, V.M. Byankin, V.Ya. Baskakov, Kristallografiya, 2o, 187 (1975)