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P. Pollmann[a]; K. Schulte[a]
[a] Institute of Physical Chemistry, University of Paderborn, Paderborn, Germany

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Behaviour of the pitch of the cholesteric and chiral smectic C helix near and at the cholesteric–smectic A–chiral smectic C multicritical point

by P. POLLMANN* and K. SCHULTE†
Institute of Physical Chemistry, University of Paderborn, D-4790 Paderborn, Germany

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A cholesteric-smectic A–chiral smectic C multicritical point was established in binary mixtures of 4-*n*-hexyloxyphenyl-4′-(2″-methylbutyl)biphenyl-4-carboxylate with cholesteryl myristate or cholesteryl benzoate. At this point the cholesteric phase, smectic A phase, and chiral smectic C phase become indistinguishable. Whereas the pitch of the cholesteric helix at the S_A–Ch phase transition is infinite already in the vicinity of the multicritical point, the pitch of the cholesteric helix at the S_C^*–Ch transition becomes infinite only at this point. In accord with the theory of Beresnev the pitch of the chiral smectic C helix remains finite at the multicritical point. Additional high pressure experiments support the results obtained at atmospheric pressure.

1. Introduction

To date much work has focused on the nematic–smectic A–smectic C multicritical point (= NAC point) in liquid crystal binary systems. At this point the lines of a second order S_A–N and S_C–S_A as well as of a first order S_C–N transition intersect, which means that the N, S_A and S_C phases become indistinguishable. In this study the achiral molecules of such systems are replaced by chiral molecules in order to find a corresponding cholesteric–smectic A–chiral smectic C multicritical point and to observe the behaviour of the pitch of the cholesteric and chiral smectic C helix near and at this point. In the following part the order of the three transitions under investigation and the behaviour of the pitch at these transitions will be briefly reviewed.

(*a*) S_A–*Ch transition*

This transition of a single compound can change from first order at atmospheric pressure to second order at elevated pressure. As long as the transition is first order, the pitch of the cholesteric helix, z, reaches only a finite value at the S_A–Ch transition. When the transition, however, crosses to second order with increasing transition pressure, z diverges ($z \rightarrow \infty$), which means a total unwinding of the cholesteric helix at the transition [1]. An analogous result can be obtained at atmospheric pressure by varying the ratio of appropriately selected components of a binary mixture [1].

(*b*) S_C^*–*Ch transition*

We have obtained a contrary result for the S_C^*–Ch transition of CE3 (see Experimental) [2], which is first order at atmospheric pressure. Since z is proportional

* Author for correspondence.
† Present address: BASF AG, ZKT, D 6700 Ludwigshafen, Germany.

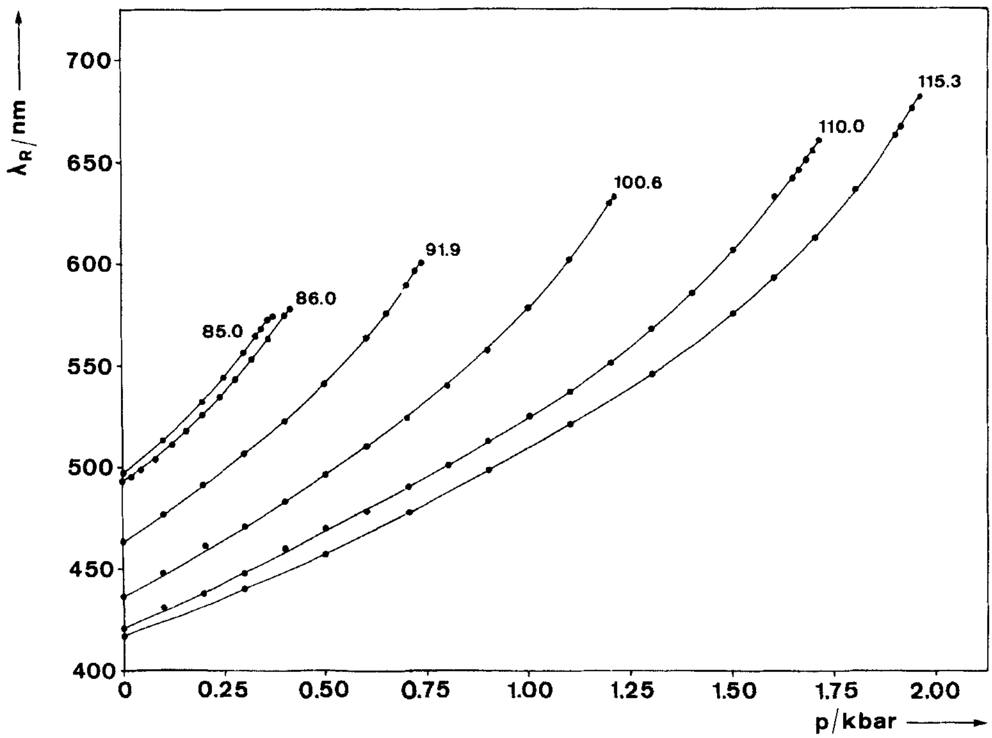

Figure 1. Wavelength of maximum light reflection, λ_R, of the CE3 Ch phase versus pressure, p, at various temperatures (the temperature is given in °C).

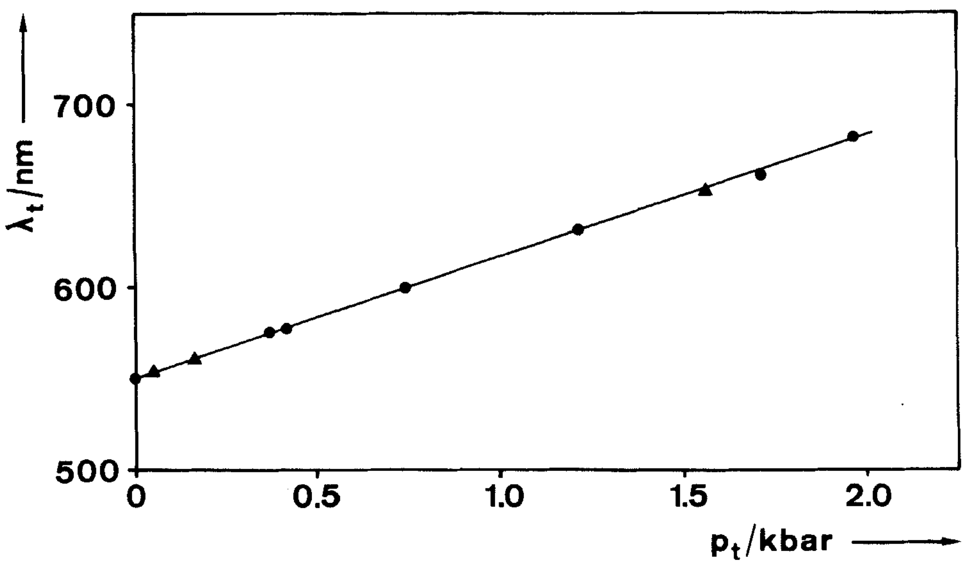

Figure 2. Wavelength of maximum light reflection at the S_C^*–Ch phase transition, λ_t, of the CE3 Ch phase versus phase transition pressure, p_t (circles: increasing pressure; triangles: decreasing pressure).

to the wavelength of maximum light reflection of the Ch phase, λ_R, we could investigate the behaviour of z near and at the S_C^*–Ch transition by light reflection measurements (see Experimental). Figure 1 shows the pressure (p) dependence of λ_R for CE3 at six temperatures. No divergence of λ_R with p is observable, all of the isotherms end at the transition of the Ch to the S_C^* phase with a finite value of λ_R, corresponding to a finite pitch. This means that the S_C^*–Ch transition of CE3 remains first order.

In the following the last (first) λ_R value in the Ch phase before (after) the transition will be denoted by λ_t. In figure 2 the six λ_t values, attainable from figure 1 obtained with increasing pressure (see circles in figure 2), and the three λ_t values obtained with decreasing pressure starting in the S_C^* phase (see triangles in figure 2) are plotted versus the phase transition pressure, p_t. Although we can see in figure 2 a linear shift of λ_t with p_t to longer wavelength, λ_t and z_t, respectively, would be infinite only at infinite p_t. Now we ask how the pitch of the cholesteric helix would behave at a possible Ch–S_A–S_C^* multicritical point where the S_C^*–Ch transition must become second order. The same interesting question is applicable to the pitch of the chiral smectic C helix, which at atmospheric as well as at elevated pressure has been found to be finite at this transition [2].

(c) S_C^*–S_A transition

As we know from the literature (see e.g. [3]) this transition can be first or second order. The pitch of the chiral smectic C helix seems always to be finite at the transition regardless of its order [4].

2. Experimental

The binary mixtures studied are composed of 4-*n*-hexyloxyphenyl-4′-(2″-methylbutyl)biphenyl-4-carboxylate (CE3) and cholesteryl myristate (CM) or cholesteryl benzoate (CB). CE3 was checked by thin layer chromatography and could be used without further purification. CM and CB were purified by repeated recrystallization from an acetone/ethanol (1 : 3) mixture.

According to the proportionality of the pitch of the cholesteric helix, z, and the wavelength of maximum light reflection of the cholesteric phase, λ_R, the pressure–temperature dependence of z could be followed with a Cary 17 DH spectrophotometer (for details see [5]). Phase transition temperatures were calorimetrically determined by a Perkin–Elmer DSC 2 and optically by a Leitz polarizing microscope provided with Mettler FP 52 hot stage and FP 5 temperature control. Measurements of transition enthalpies were also carried out with a Perkin–Elmer DSC 2.

3. Results

In order to find a Ch–S_A–S_C^* multicritical point at atmospheric pressure it seemed to be promising to mix two components one of which has a S_C^*–Ch and the other one a S_A–Ch phase transition. For that reason 4-*n*-hexyloxyphenyl-4′–(2″-methylbutyl)biphenyl-4-carboxylate, which exhibits a S_C^*–Ch transition, was mixed with cholesteryl myristate, which has a S_A–Ch transition. In addition CE3 was mixed with cholesteryl benzoate to have an induced S_A–Ch transition, too; CB itself has only a Ch phase. Figures 3 and 4 give the temperature–concentration (T–x) diagrams obtained. As can be seen in both diagrams, the S_C^*–Ch, S_A–Ch, and S_C^*–S_A transition lines intersect at about a mole fraction $x_{CM}=0{\cdot}15$ and $x_{CB}=0{\cdot}19$, respectively. In the following the orders of these three transitions will be considered.

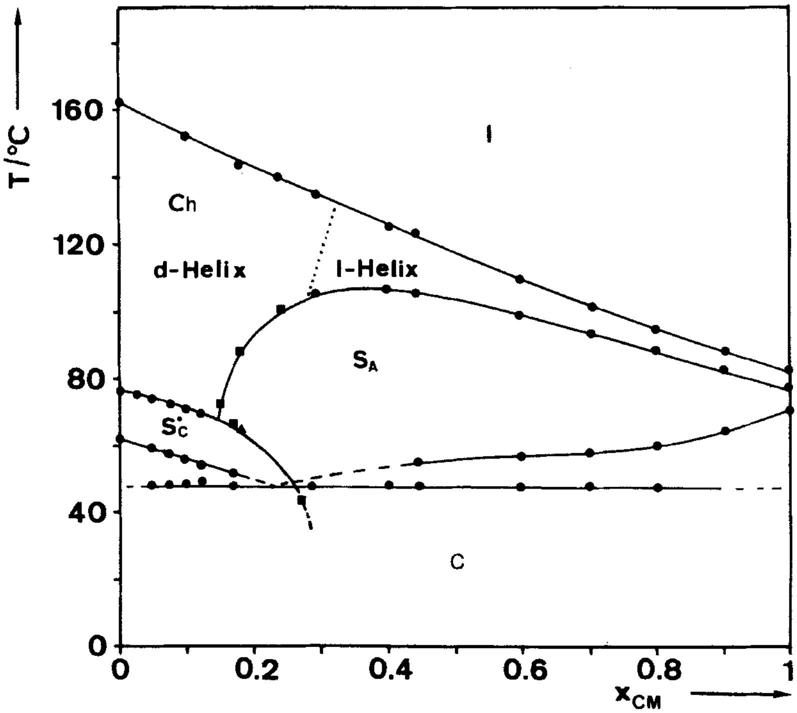

Figure 3. Temperature–concentration (T–x) diagram of the CE3/CM binary system (circles: calorimetric; squares: microscopy; triangles: light reflection).

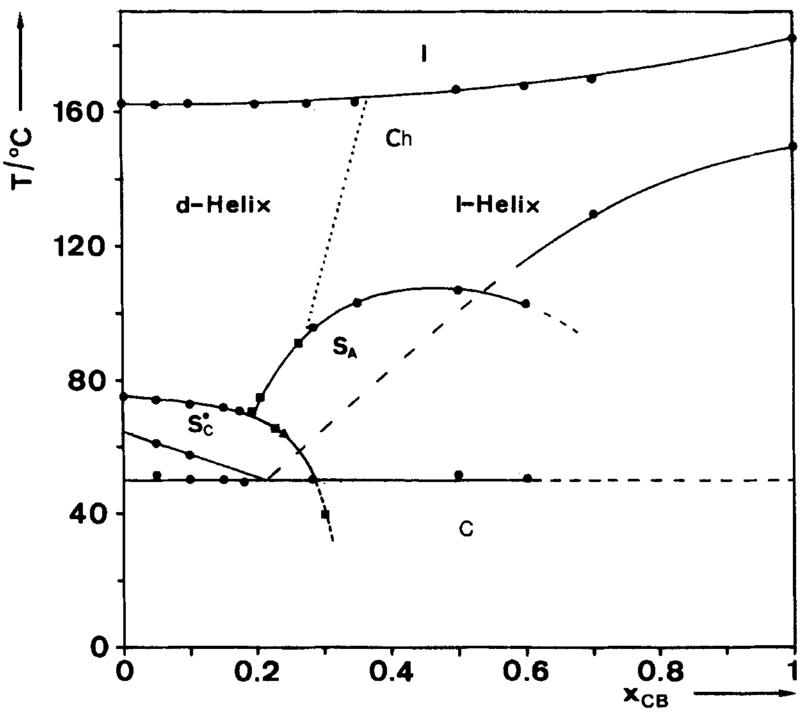

Figure 4. Temperature–concentration (T–x) diagram of the CE3/CB binary system (circles: calorimetric; squares: microscopy; triangles: light reflection).

(*a*) S_A–*Ch transition*

Here a small complication arises. CE3 forms a right handed, while CM and CB form a left handed cholesteric helix, so that a helix inversion line [6] occurs in the Ch phase (see dotted line in figures 3 and 4). The coexisting Ch phase near the intersection point is a right handed one.

Figure 5 shows that $\Delta_t H$, the change in enthalpy of the S_A–Ch transition, becomes zero at the mole fraction of the intersection point, $x_{CM} = 0{\cdot}15$. $\Delta_t H$ in the vicinity of that point represents a pretransitional enthalpy effect, because the S_A–Ch transition is already second order at x_{CM} of 0·4 (see [7]). Light reflection measurements establish a S_A–Ch tricritical point at this mole fraction (the details are given later). Thus the discontinuous part of the total transitional enthalpy disappears at this tricritical point. For the CE3/CB system no dependence of $\Delta_t H$ on x_{CB} could be obtained. Close to the intersection point no enthalpy effect was detectable, only at $x_{CB} \approx 0{\cdot}27$ was a small value ($< 50\ \mathrm{J\,mol^{-1}}$) measured. Above this mole fraction $\Delta_t H$ remains nearly constant. In order to determine the transition line very close to the intersection point as accurately as possible, transition points were observed by a polarizing microscope (see squares in figures 3 and 4).

(*b*) S_C^*–*Ch transition*

$\Delta_t H$ of the S_C^*–Ch transition of both binary systems decreases with increasing mole fraction of CM and CB, and in both cases becomes zero at the intersection point (see figures 5 and 6, respectively).

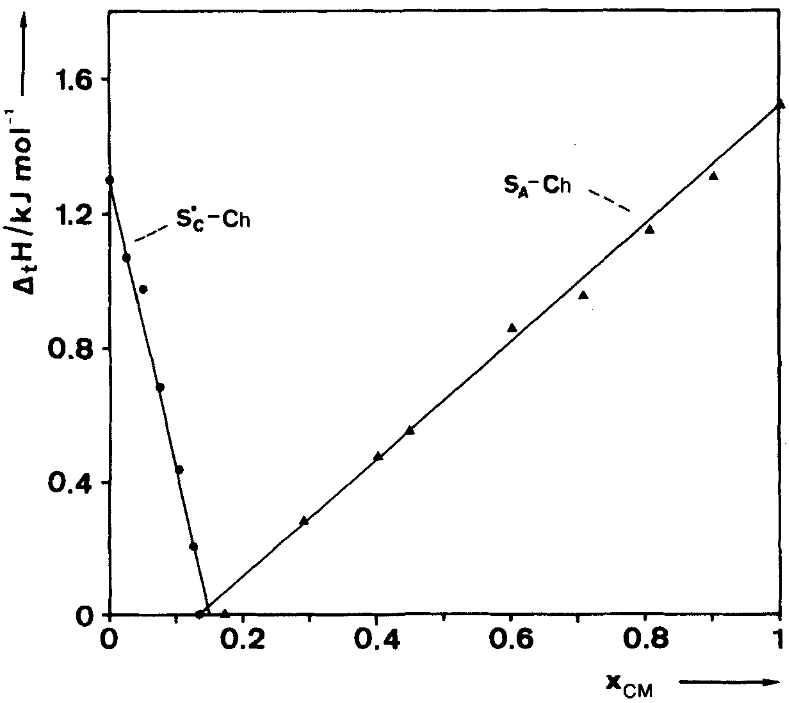

Figure 5. S_C^*–Ch and S_A–Ch transitional enthalpy, $\Delta_t H$, of the CE3/CM binary system versus CM mole fraction, x_{CM}.

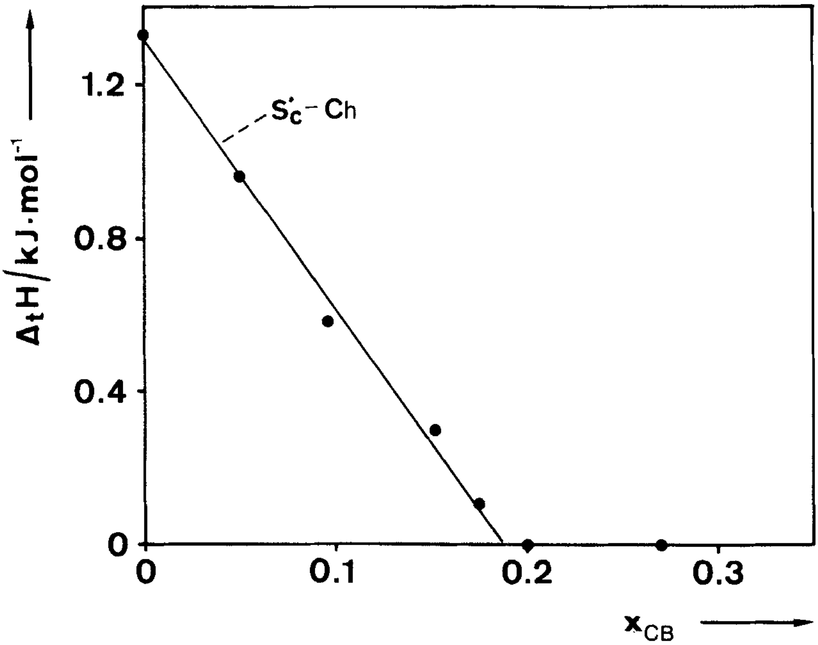

Figure 6. S_C^*–Ch transitional enthalpy, $\Delta_t H$, of the CE3/CB binary system versus CB mole fraction, x_{CB}.

(c) S_C^*–S_A transition

No enthalpy effect could be detected along the S_C^*–S_A phase boundary of both binary systems, which was determined by optical microscopy.

From such observations it follows that the Ch–S_A–S_C^* intersection point in figures 3 and 4, respectively, is a multicritical point, where the Ch, S_A and S_C^* phases become indistinguishable. The behaviour of the pitch of the cholesteric helix in the vicinity of the multicritical point was investigated further by means of λ_R, the wavelength of maximum light reflection of the cholesteric phase, which is proportional to the pitch. Well above the multicritical point in the CE3/CM system, the $\lambda_R = f$(temperature) isobars (1 bar) end with a finite λ_t at the S_A–Ch transition indicating that the transition is first order. With decreasing x_{CM} λ_t increases pointing to a tricritical point, although the system is simultaneously approaching the helix inversion line. An extrapolation procedure in figure 7 establishes $\lambda_t^{-1} = 0$ and $\lambda_t = \infty$, respectively, at x_{CM} of 0·4. That means the helix is totally unwound ($z = \infty$) at the S_A–Ch phase boundary and the transition has become second order. λ_t remains infinite until the multicritical point. A tricritical behaviour of the transition of the Ch phase into the induced S_A phase of the CE3/CB system could not be established, because λ_t is beyond the measuring range of the spectrophotometer used in this study. Since $\Delta_t H$ of this transition is very low, already well above the multicritical point, a tricritical point is most probable, so that an infinite pitch of the cholesteric helix at the multicritical point can be assumed in this case, also.

Approaching the multicritical point along the S_C^*–Ch transition line with increasing x_{CM}, we find a breaking-off behaviour of the $\lambda_R = f$(temperature) isobars (1 bar) in the Ch phase at the S_C^*–Ch transition, as is the case for the S_A–Ch transition above the

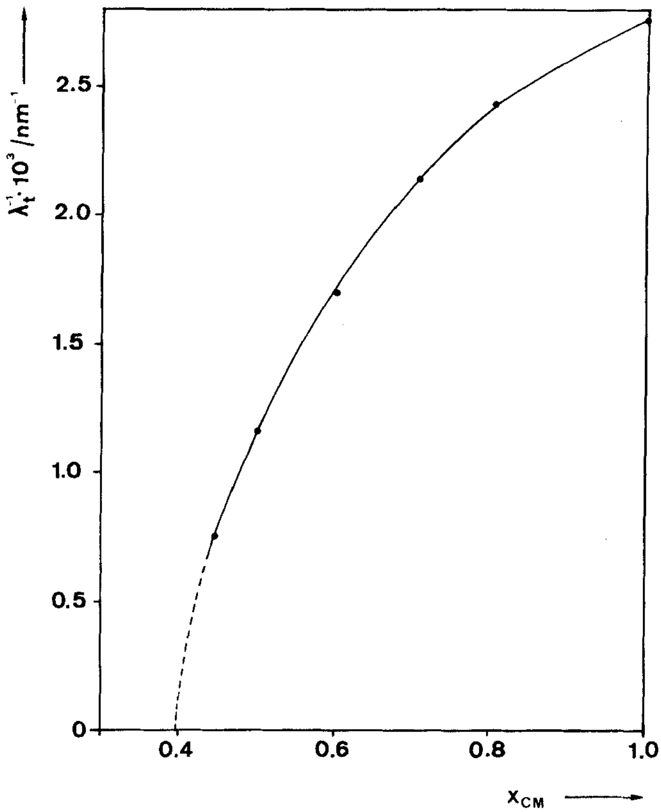

Figure 7. Reciprocal of the wavelength of maximum light reflection at the S_A–Ch phase transition, λ_t^{-1}, of the CE3/CM binary system versus CM mole fraction, x_{CM}.

tricritical point. Plotting λ_t^{-1} as a function of x_{CM}, as seen in figure 8, λ_t^{-1} first decreases linearly. At higher x_{CM}, however, it seems to depart from the linearity and tends towards zero ($\lambda_t \rightarrow \infty$) at about the mole fraction of the multicritical point ($x_{CM} = 0{\cdot}15$).

In the CE3/CB system only a linear decrease of λ_t^{-1} was found (see figure 9). An extrapolation to $\lambda_t^{-1} = 0$ would lead to a mole fraction somewhat higher than that of the multicritical point ($x_{CB} = 0{\cdot}19$). In order to support these results some additional high pressure measurements of λ_t were undertaken. As mentioned in the Introduction, λ_t of CE3 in the Ch phase at the S_C^*–Ch transition increases linearly with increasing transition pressure, p_t (see figure 2). On mixing CE3 with CM and CB, respectively, the slope of the $\lambda_t = f(p_t)$ lines rises when the CM and CB content increases (see figures 10 and 11). In figure 12 $(d\lambda_t/dp_t)^{-1}$ is plotted versus x_{CM} and x_{CB}. An extrapolation of both curves to $(d\lambda_t/dp_t)^{-1} = 0$ yields fairly precisely the mole fraction of the multicritical point in the CE3/CM ($x_{CM} = 0{\cdot}15$) and CE3/CB system ($x_{CB} = 0{\cdot}19$), respectively. This result is consistent with the earlier one, where the pitch was found be be infinite only at the multicritical point. As shown earlier for the S_A–Ch transition the pitch is already infinite in the vicinity of the multicritical point.

Finally, the behaviour of the pitch of the chiral smectic C helix in the vicinity of the multicritical point was studied, again by means of λ_R. At light incidence parallel to the helix axis λ_R is proportional to the pitch of the helix as for the cholesteric helix. It was

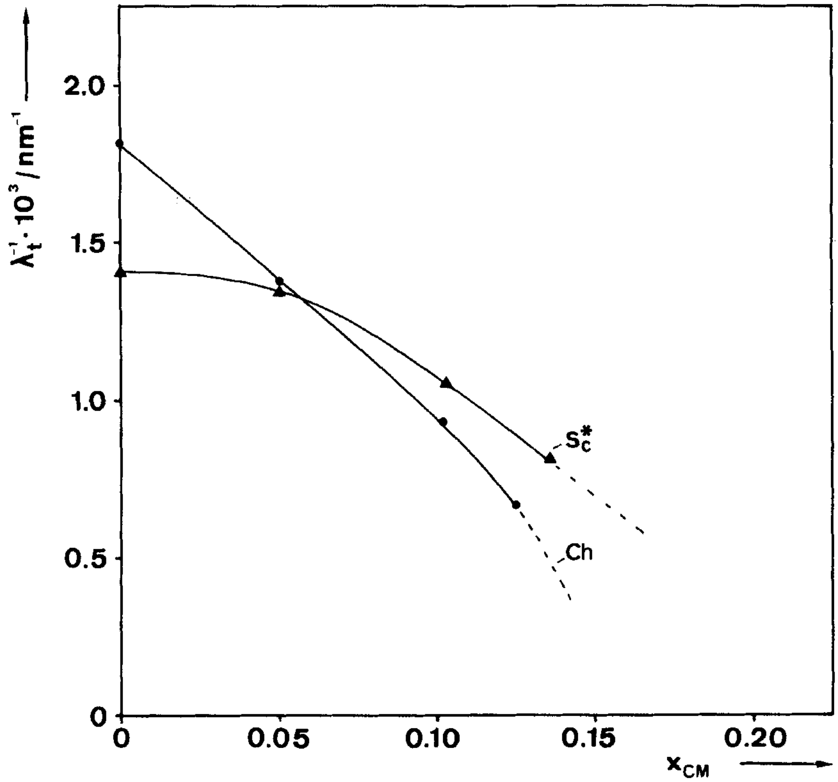

Figure 8. Reciprocal of the wavelength of maximum light reflection at the S_C^*–Ch phase transition in the Ch (circles) and in the S_C^* phase (triangles), λ_t^{-1}, of the CE3/CM binary system versus CM mole fraction, x_{CM}.

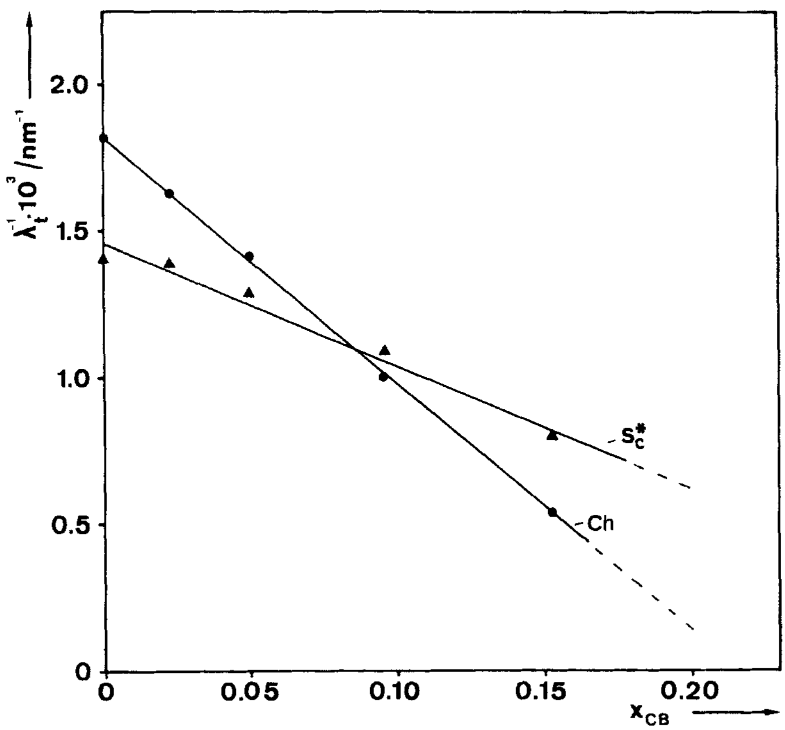

Figure 9. Reciprocal of the wavelength of maximum light reflection at the S_C^*–Ch phase transition in the Ch (circles) and in the S_C^* phase (triangles), λ_t^{-1}, of the CE3/CB binary system versus CB mole fraction, x_{CB}.

found that the measured $\lambda_R = f$(temperature) isobars (1 bar) in the S_C^* phase of the CE3/CM system exhibit a breaking-off behaviour at the transition. Plotting now λ_t^{-1} versus x_{CM} (see figure 8), λ_t^{-1} does not become zero, when extrapolated to $x_{CM} = 0{\cdot}15$, the familiar mole fraction of the multicritical point. The same result was obtained in the CE3/CB system, with the multicritical point at x_{CB} of 0·19 (see figure 9). From this we conclude that contrary to the pitch of the cholesteric helix the pitch of the chiral smectic C helix remains finite at the multicritical point.

Since the line of the second order S_C^*–S_A transition of both systems ends at the multicritical point also, the pitch of the chiral smectic C helix at this transition must remain finite as well. This behaviour of the pitch follows the theory by Beresnev *et al.* [4], but does not support the theoretical explanation given by Goossens [8]. According to Goossens, not only the tilt angle but also the pitch should approach zero at the S_C^*–S_A transition. Unfortunately, in our study the pitch at the S_C^*–S_A transition could not be determined, since the corresponding λ_t was beyond the measuring range of the

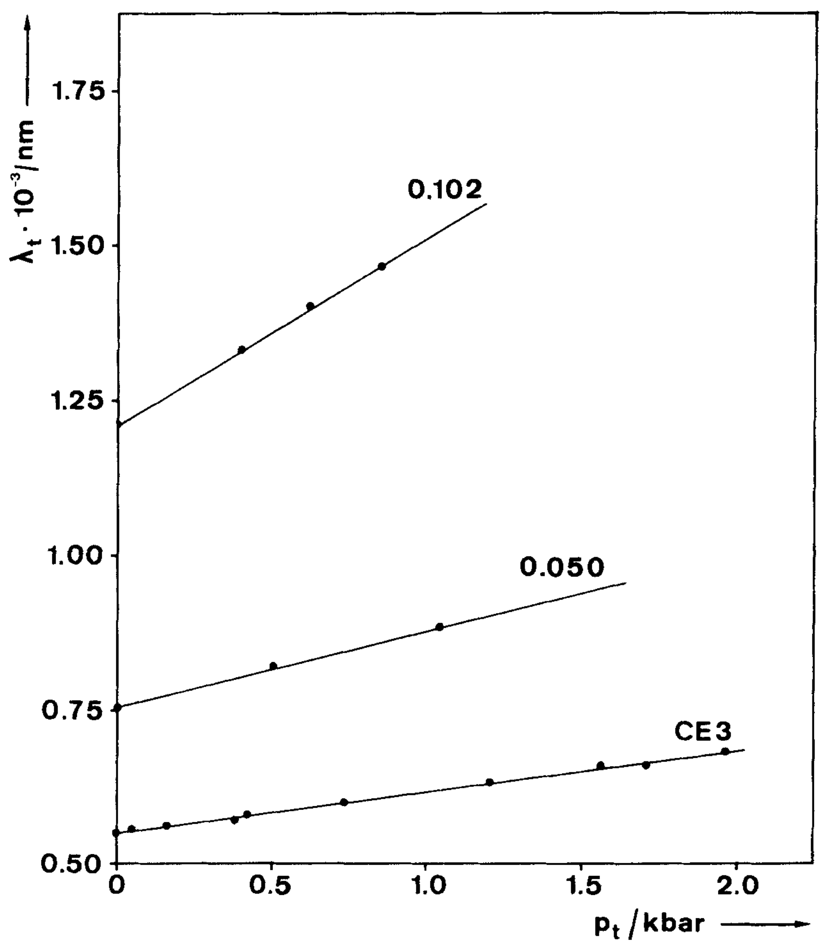

Figure 10. Wavelength of maximum light reflection at the S_C^*–Ch phase transition in the Ch phase, λ_t, for various CM mole fractions of the CE3/CM binary system versus phase transition pressure, p_t.

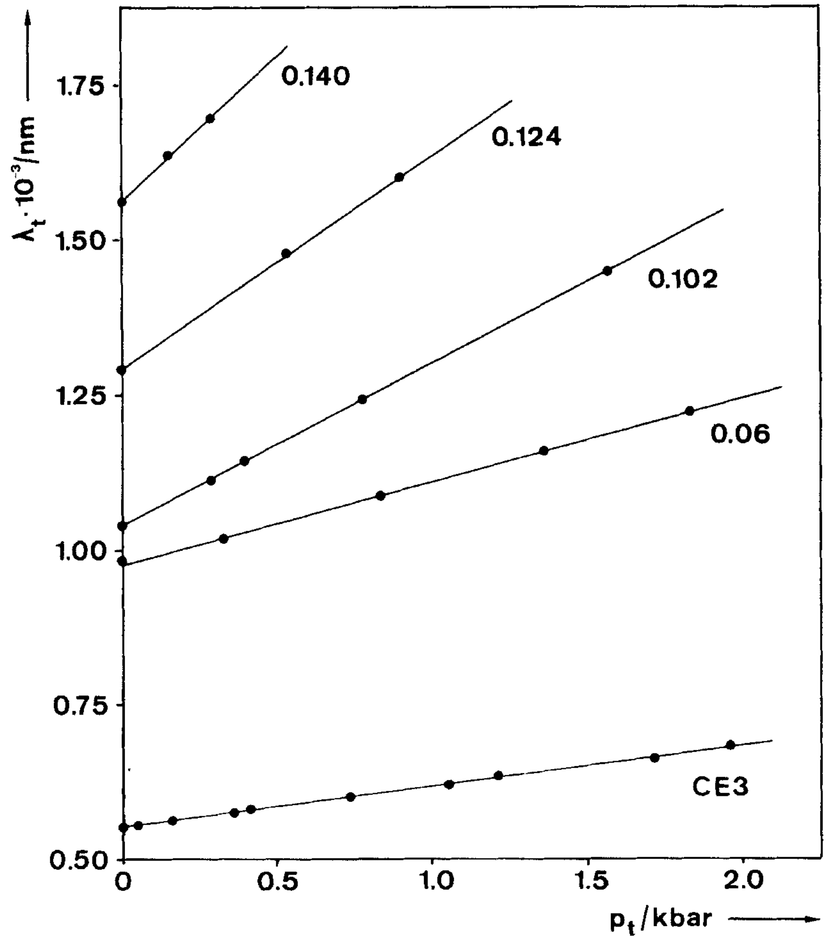

Figure 11. Wavelength of maximum light reflection at the S_C^*–Ch phase transition in the Ch phase, λ_t, for various CB mole fractions of the CE3/CB binary system versus phase transition pressure, p_t.

spectrophotometer. As far as we know from experiments reported in the literature, it is true that the pitch decreases when the temperature approaches the transition temperature, but it remains finite at the transition point.

By using mole fractions not far above the multicritical point the reflection band could at least be measured quite close to the transition. Since theory tells us [9] that the intensity of the band disappears at the transition to the S_A phase, we determined the temperature of the S_C^*–S_A transition by extrapolating the intensity as a function of temperature to zero (see triangles in figures 3 and 4).

In connection with the behaviour of the cholesteric helix near and at the multicritical point already mentioned, the paper by Lubensky and Renn [10] is of great interest. They predict theoretically a 'twisted grain boundary' phase between the S_A and Ch phase near this multicritical point. We believe that the presence of a twisted grain boundary phase in our case can be ruled out, because a tricritical point of the

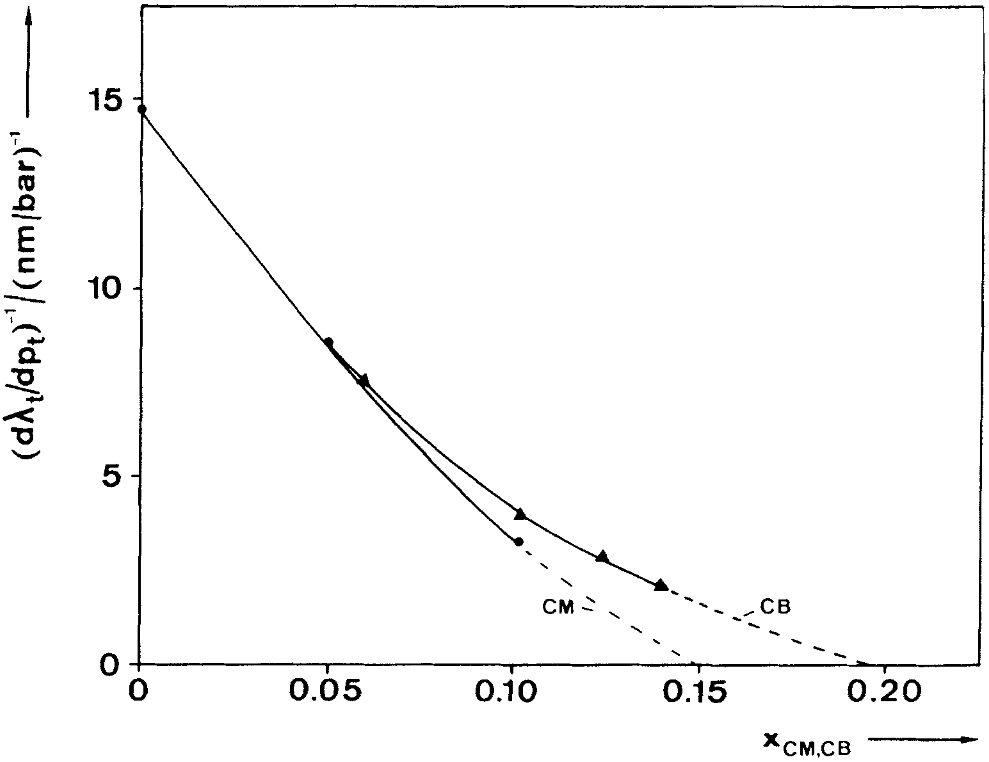

Figure 12. Reciprocal of the slopes of the lines in figures 10 and 11 $(d\lambda_t/dp_t)^{-1}$, versus CM (circles), and CB (triangles), respectively, mole fraction.

S_A–Ch transition has been found relatively far away from the multicritical point which means an untwisted cholesteric helix along the S_A–Ch phase boundary from the tricritical point until the multicritical point, which would not allow the existence of a twisted grain boundary phase.

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