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Pressure-induced re-entrant cholesteric phase behaviour of non-polar liquid crystals

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In a previous paper we reported the existence of a pressure-induced re-entrant cholesteric phase in mixtures of non-polar liquid crystals. Now the influence of the mixing ratio on this behaviour has been studied up to 3000 bar and 190°C and the phase boundaries based on light reflection measurements have been confirmed by transmission and texture observations in a diamond anvil cell. Additional thermodynamic investigations show that when the cholesteric/smectic A phase transition line possesses a maximum temperature the pretransition enthalpy and volume disappear.

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1. Introduction

Re-entrant polymorphism in liquid-crystalline materials was first observed by Cladis [1]. On decreasing temperature a binary mixture of two terminal polar compounds shows the phase sequence nematic, smectic-A and again nematic. Subsequently re-entrant nematic phases were discovered in pure compounds at normal [2] and high pressure [3]. Accordingly, re-entrant nematic behaviour seemed to occur only in para-cyano substituted compounds for which the smectic A phase is of the bilayer type (S_{A_d}). With decreasing temperature (corresponding to increased pairing) the S_{A_d} phase becomes unstable against the nematic phase because of the unfavourable packing of the bulky dimers.

However, re-entrant nematic behaviour was also observed in binary systems of two terminal non-polar compounds [4–6] and pressure-induced re-entrant cholesteric phases were revealed in ternary mixtures of weakly polar cholesteryl *n*-alkanoates [7]. In this work, the p,T cholesteric/smectic A (Ch/S_A) phase boundaries of six ternary mixtures of cholesteryl nonanoate (Ch-9), tetradecanoate (Ch-14) and propionate (Ch-3) obtained from light reflection measurements in the cholesteric phase are presented. Calorimetric and volumetric studies of these mixtures were performed at normal pressure. Additionally phase transitions and textures were studied under pressure in a diamond anvil cell using a high pressure polarizing microscope.

2. Experimental

The wavelength of maximum light reflection λ_R in the cholesteric Grandjean texture was determined with a Cary 17 DH spectrophotometer (Varian). For this purpose the sample was oriented between two spectrosil disks with a layer thickness of 23 μm. Details of the high pressure equipment have been described earlier [8]. For the calorimetric measurements a differential scanning calorimeter (D.S.C.-2, Perkin–Elmer) was used. The D.S.C. runs were taken on heating with 4 to 10 mg samples of mixtures. The temperature dependence of the molar volume was determined with the digital density device DMA 02 D using the measuring cell DMA 601 HT from Paar/Heraeus. In this apparatus the molar volume is obtained from the resonance frequency of an electronically stimulated bending vibrator, which is filled with the sample [9]. The diamond anvil cell used for the high pressure measurements is described elsewhere [10–12]. Cholesteric and smectic textures were observed using a polarizing microscope. The phase transitions were indicated by a change of the intensity of the polarized light transmitted through the sample. To produce a homeotropic orientation of the S_A phase (and thus to increase the change of intensity during the phase transition) the diamond surfaces were coated with the surfactant HTAB (hexadecyltrimethyl-ammonium bromide). During a phase transition the heating and cooling rates were generally 0·5 K min^{-1}. The pressure was determined within ± 150 bar by an internal pressure calibration (for details see [10, 12]) using data obtained from D.T.A. (Ch/I (isotropic) transition, Kleinhans [13]) and λ_R measurements (this work).

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3. Results

In the eutectic mixture of the two smectic cholesteryl *n*-alkanoates Ch-9 and Ch-14 with a mole fraction ratio of $x_{Ch\text{-}9}/x_{Ch\text{-}14}$ = 2·11, the Ch/S_A phase transition occurs at 71·3°C at normal pressure [14]. By adding a cholesteryl *n*-alkanoate (Ch-3), which has

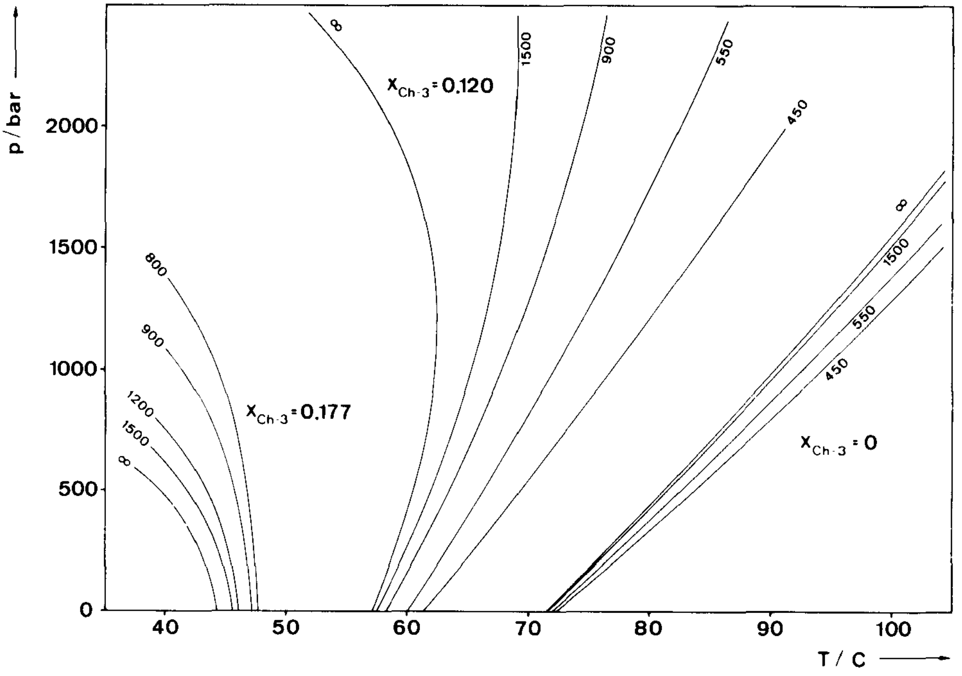

Figure 1. Isochroms (numerical data in nm) of the cholesteric phase of three ternary Ch-9/Ch-14/Ch-3 mixtures; mole fraction ratio $x_{Ch\text{-}9}/x_{Ch\text{-}14}$ = 2·11.

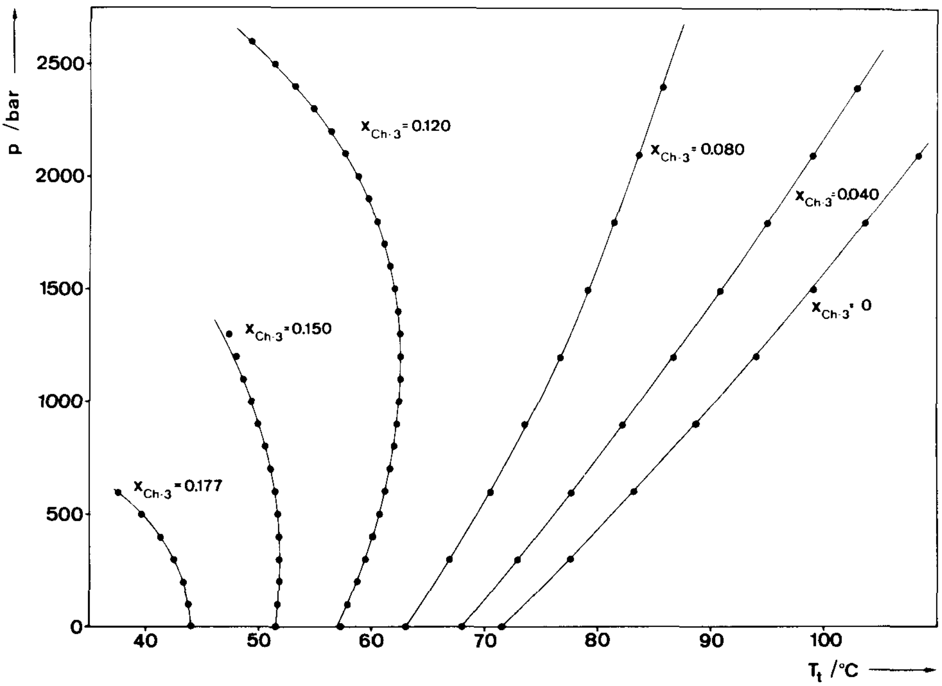

Figure 2. p,T_t Ch/S$_A$ phase boundaries of the ternary system Ch-9/Ch-14/Ch-3; $x_{Ch\text{-}9}/x_{Ch\text{-}14} = 2{\cdot}11$.

a significantly shorter *n*-alkyl chain and no S$_A$ phase, six ternary mixtures were prepared. Their p,T phase boundaries (cf. figure 2) were obtained from light reflection measurements in their cholesteric phases (cf. figure 1). From the isochroms (lines of constant λ_R) of the cholesteric phase shown in figure 1 the phase transition temperature T_t at constant pressure can be determined using the function

$$\lambda_R = A(T/T_t - 1)^{-B},$$

(for details see [15]). λ_R becomes infinite at T_t because the Ch/S$_A$ phase transition of the mixtures is continuous (see later). The phase boundaries for the mixtures with $x_{Ch\text{-}3} = 0{\cdot}120$ and $0{\cdot}150$ exhibit a maximum temperature and accordingly a pressure-induced re-entrant cholesteric (Ch$_{re}$) phase. For example, the mixture with $x_{Ch\text{-}3} = 0{\cdot}120$ shows the phase sequence

$$\mathrm{Ch} \xrightarrow{395\,\mathrm{bar}} \mathrm{S_A} \xrightarrow{1855\,\mathrm{bar}} \mathrm{Ch_{re}}$$

at 60°C. No pressure maximum of the phase boundaries was found, which is in contrast to the re-entrant behaviour for nematic phases of polar compounds [16].

In addition, the slope dT_t/dp of the phase boundaries at normal pressure decreases with increasing mole fraction of Ch-3 and becomes zero at $x_{Ch\text{-}3} = 0{\cdot}172$. We have studied therefore the thermodynamic properties of this ternary system at normal pressure. In figure 3 the isobars of the molar volume ($V(T)$) and thermal expansion coefficient ($\alpha(T)$) of three mixtures are presented. The $V(T)$ isobars reveal, that the Ch/S$_A$ phase transitions of all mixtures are most probably continuous (critical). The possible extent of a two phase region is estimated in the Discussion. The pretransition

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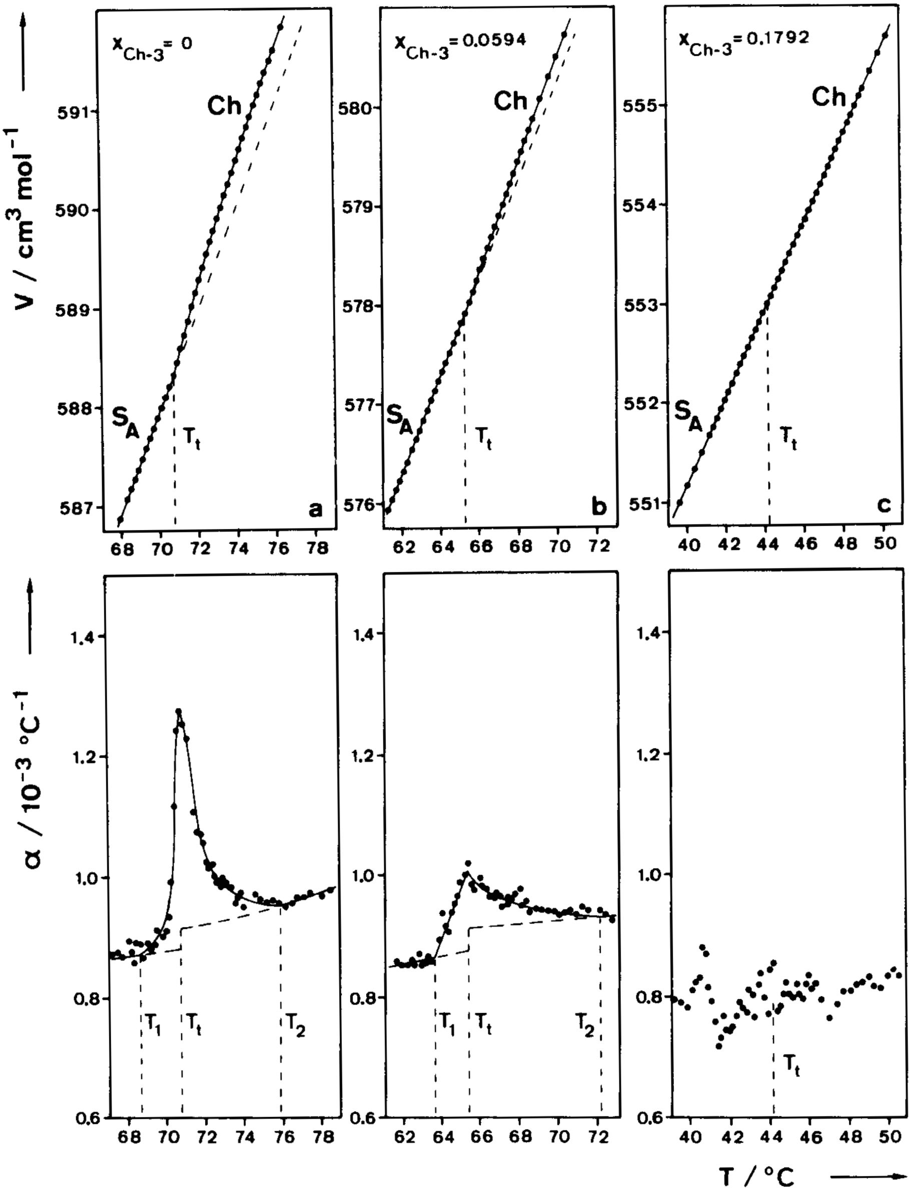

Figure 3. Molar volume, V, and thermal expansion coefficient, α, of three Ch-9/Ch-14/Ch-3 mixtures at normal pressure versus temperature, T; $x_{\text{Ch-9}}/x_{\text{Ch-14}} = 2{\cdot}11$.

volume $\Delta_t V$ in the pretransition region between T_1 and T_2 can be derived exactly by integration of the $\alpha(T)$ isobars,

$$\Delta_t V = V \int_{T_1}^{T_2} \alpha(T)\,dT;$$

assuming the molar volume V is nearly constant.

The D.S.C. runs of three mixtures given in figure 4 show that the Ch/S_A phase transition is an unsymmetrical λ transition with weak pretransitional effects in the S_A

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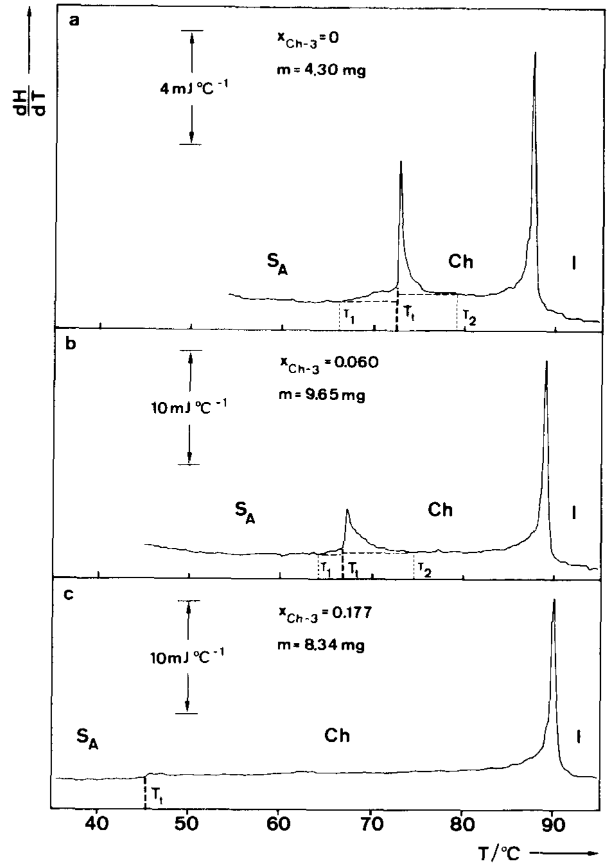

Figure 4. D.S.C. runs of three Ch-9/Ch-14/Ch-3 mixtures at normal pressure; $x_{Ch\text{-}9}/x_{Ch\text{-}14} = 2{\cdot}11$; heating rate: $5\,K\,min^{-1}$.

phase (T_l to T_t) and stronger effects in the cholesteric phase (T_t to T_2). The pretransition enthalpy $\Delta_t H$ is calculated similarly to $\Delta_t V$ by integration of the D.S.C.-thermograms

$$\Delta_t H = (\bar{M}/m)\int_{T_l}^{T_2}(dH/dT)\,dT$$

above the baseline indicated. Here $\bar{M}$ denotes the mean molar mass and m the mass of the mixture. Both, $\Delta_t V$ and $\Delta_t H$, decrease with increasing mole fraction of Ch-3 and become zero at $x_{Ch\text{-}3} = 0{\cdot}180$ (see figure 5). At nearly the same mole fraction ($x_{Ch\text{-}3} = 0{\cdot}172$) dT_t/dp of the Ch/S$_A$ phase boundary becomes zero ($\alpha p/\alpha T_t = \infty$; see figure 2).

To confirm the phase boundary Ch/S$_A$ obtained from λ_R measurements by the extrapolation method, the p,T phase diagram of the mixture with $x_{Ch\text{-}3} = 0{\cdot}120$ was also determined using a high pressure polarizing microscope (cf. figure 6). Due to the rigid gasket in the diamond anvil cell, isochors were measured (see for example a, b, c and d in figure 6), which are nearly parallel and, in particular, do not intersect. Consequently the re-entrant behaviour of the mixture can be confirmed. The phase transition temperatures obtained in cooling (Ch/S$_A$) and heating (S$_A$/Ch) runs differ remarkably by 1 to 6 K. Even at normal pressure a difference of 0·4 K was observed

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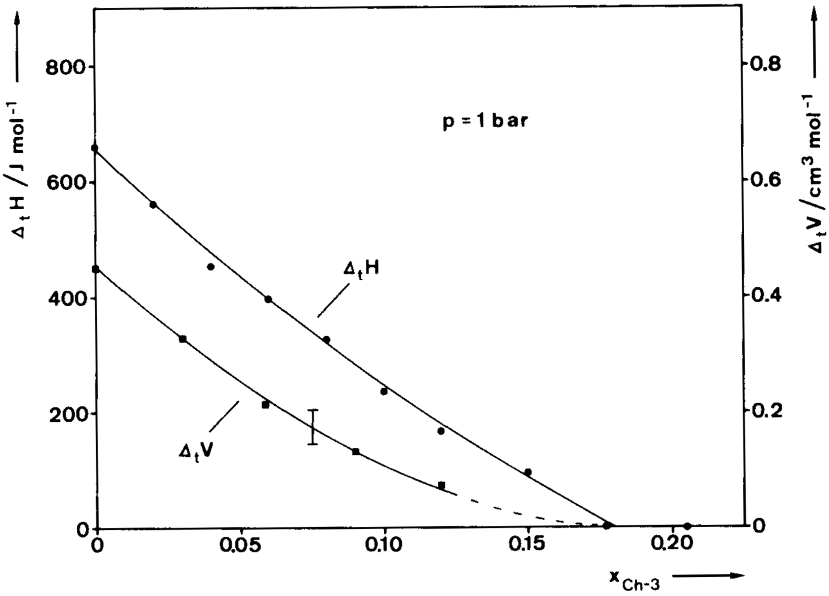

Figure 5. Pretransition enthalpy, $\Delta_t H$, and volume, $\Delta_t V$, of the Ch/S_A phase transition at normal pressure versus mole fraction, x_{Ch-3}; x_{Ch-9}/x_{Ch-14} = 2·11.

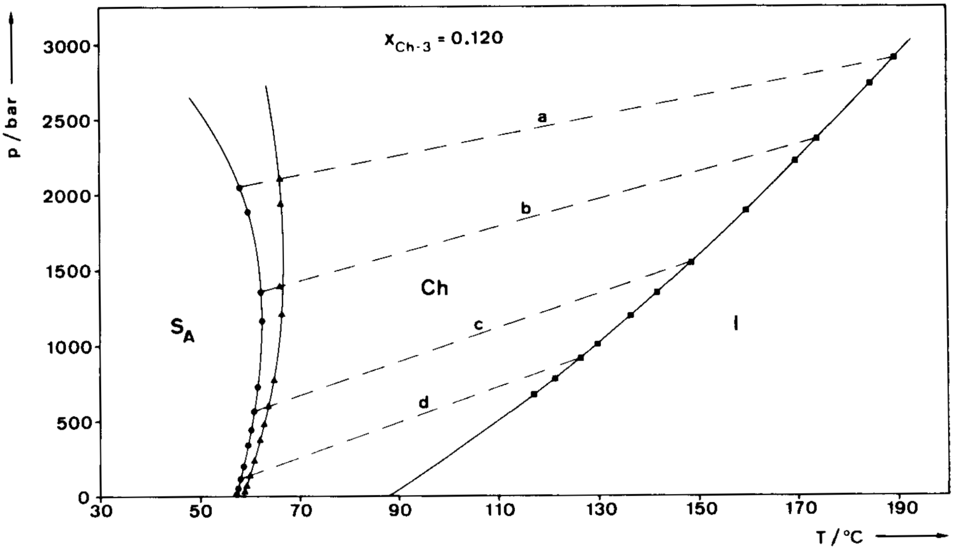

Figure 6. p,T phase diagram and isochors a, b, c, d of the ternary mixture with x_{Ch-3} = 0·120 obtained by the optical transmission technique; x_{Ch-9}/x_{Ch-14} = 2·11; Ch/S_A phase transition points detected on heating (▲) and cooling (●).

on heating stages in both laboratories using freshly prepared samples. This phenomenon has not been reported up to now, neither for the pure substances nor for mixtures containing only long chain alkanoates at normal pressure (for example, Ch-9/Ch-14 mixtures [14]) and high pressure (for example, pure Ch-14 [12, 13]). This difference does not depend on heating or cooling rates (but of course increasing rates decrease the accuracy of measurement). Even prolonged annealing in the pretransition

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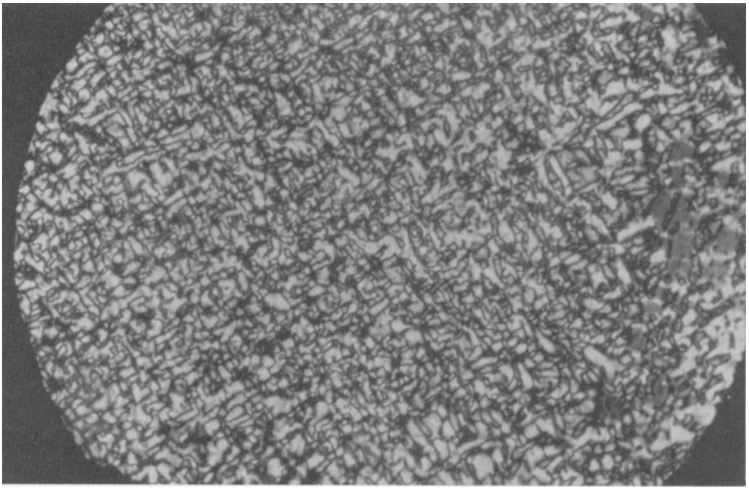

Figure 7. Cholesteric focal conic texture with a small planar area of the mixture with $x_{\mathrm{Ch}\text{-}3} = 0{\cdot}120$; $x_{\mathrm{Ch}\text{-}9}/x_{\mathrm{Ch}\text{-}14} = 2{\cdot}11$; diamond surfaces coated with HTAB; $T = 59{\cdot}4°\mathrm{C}$; $p = 200\,\mathrm{bar}$.

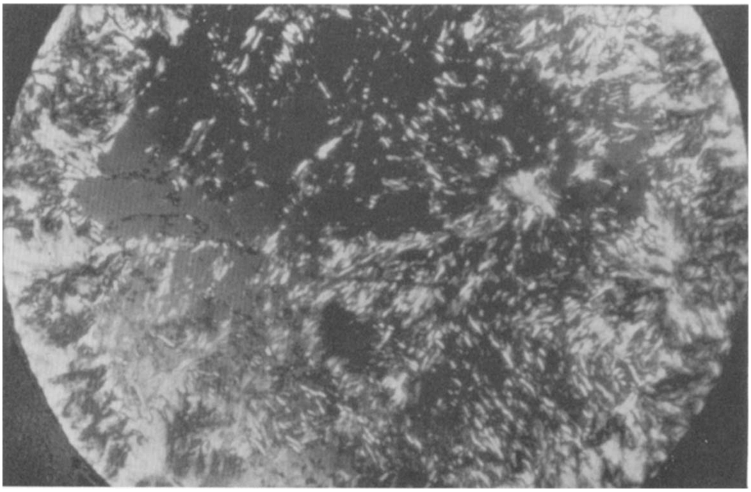

Figure 8. $\mathrm{S_A}$ homeotropic texture (only partly) of the mixture with $x_{\mathrm{Ch}\text{-}3} = 0{\cdot}120$; $x_{\mathrm{Ch}\text{-}9}/x_{\mathrm{Ch}\text{-}14} = 2{\cdot}11$; diamond surfaces coated with HTAB; $T = 59{\cdot}7°\mathrm{C}$; $p = 1700\,\mathrm{bar}$.

regions on both sides of the boundary does not affect the transition temperatures, whether or not surfactant was applied to the diamond surfaces [12].

At this time a final explanation for the differing phase transition temperatures cannot be given. Supercooling can be excluded because the phase transitions are continuous. The cholesteric and $\mathrm{S_A}$ phase at normal and high pressure were identified by a polarizing microscope. The observed textures shown in figures 7–9 also confirm the pressure-induced re-entrant cholesteric behaviour.

4. Discussion

A thermodynamic description of the $\mathrm{Ch/S_A}$ phase transition of the ternary system investigated at normal pressure follows. First of all the $\mathrm{Ch/S_A}$ two-phase region of

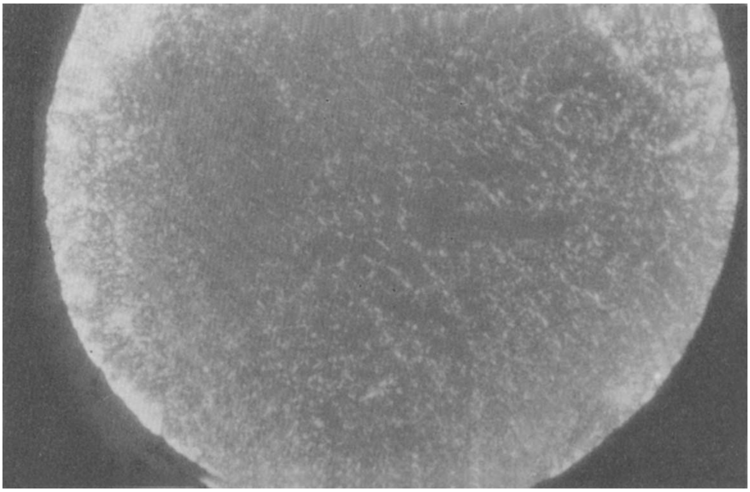

Figure 9. Cholesteric Grandjean texture of the mixture with $x_{\mathrm{Ch\text{-}3}} = 0{\cdot}120$; $z_{\mathrm{Ch\text{-}9}}/x_{\mathrm{Ch\text{-}14}} = 2{\cdot}11$; uncoated diamond surfaces; $T = 59°\mathrm{C}$; $p = 2100\,\mathrm{bar}$.

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the binary Ch-9/Ch-14 mixture must be estimated. For an ideal binary mixture a calculation using the phase transition enthalpies ($\Delta_t H_{\mathrm{Ch\text{-}9}} = 444\,\mathrm{J\,mol^{-1}}$; $\Delta_t H_{\mathrm{Ch\text{-}14}} = 1500\,\mathrm{J\,mol^{-1}}$ [17]) and temperatures ($T_{\mathrm{Ch\text{-}9}} = 349{\cdot}0\,\mathrm{K}$; $T_{\mathrm{Ch\text{-}14}} = 352{\cdot}0\,\mathrm{K}$) of the pure compounds yields a very small two-phase region of 0·002 K for this mixture ($x_{\mathrm{Ch\text{-}9}} = 0{\cdot}678$). Therefore the two-phase regions of the ternary mixtures may also be neglected. Accordingly the Ehrenfest equations for second order phase transitions

$$dT_t/dp = VT_t\Delta\alpha/\Delta C_p, \tag{1}$$

$$dT_t/dp = \Delta\chi/\Delta\alpha, \tag{2}$$

can be applied in this case. The Ch/S$_A$ phase transition of the mixture where $dT_t/dp = 0$ or $dp/dT_t = \infty$ ($x_{\mathrm{Ch\text{-}3}} = 0{\cdot}172$) is very interesting. Since $\Delta C_p = C_{p(\mathrm{Ch})} - C_{p(\mathrm{S_A})} > 0$ (see figure 4(*c*)), it follows from equation (1) that $\Delta\alpha = 0$ and thus from equation (2) that $\Delta\chi = 0$. Furthermore, it is reasonable to conclude that under these conditions the pretransition volume $\Delta_t V$ and enthalpy $\Delta_t H$ of the Ch/S$_A$ transition disappear.

Analogous thermodynamic behaviour is observed for the isothermal nematic/smectic A phase transitions of 8OCB (4-*n*-octyloxy-4′-cyano biphenyl) at high pressure. The pretransition enthalpy of this continuous phase transition is $100\,\mathrm{J\,mol^{-1}}$ at normal pressure. It decreases with increasing pressure and becomes zero in the same pressure region (1500–2000 bar) where the slope dT_t/dp of the phase boundary becomes zero [18].

We have additional experimental evidence that by adding the short-chain Ch-3 to the eutectic Ch-9/Ch-14 mixture a positive excess volume occurs in the S$_A$ phase. Based on this effect, an explanation of the pressure-induced re-entrant cholesteric behaviour will be given in a future paper.

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