Effect of composition on the pressure-induced re-entrant cholesteric phase behaviour of mixtures of non-polar cholesteryl *n*-alkanoates

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Recently we reported a pressure-induced re-entrant cholesteric phase for ternary systems of non-polar cholesteryl *n*-alkanoates. In these systems one component contains a shorter *n*-alkyl chain than the other two. We now show that the former produces a positive excess volume in the smectic phase, which is probably responsible for the pressure-induced re-entrant phase behaviour. The maximum temperature of the cholesteric/smectic A phase boundary is found to decrease drastically with decrease of the *n*-alkyl chain length of this particular component.

1. Introduction

In a preceding publication [1] we have reported a pressure-induced re-entrant cholesteric phase for mixtures of three non-polar cholesteryl *n*-alkanoates: cholesteryl propionate (Ch-3), nonanoate (Ch-9), and tetradecanoate (Ch-14). The cholesteric/smectic A (Ch/S_A) phase boundary exhibited a maximum in the temperature (cf. figure 1), which means that the slope of the boundary $(\partial p_t/\partial T_t)$ is infinite and $(\partial T_t/\partial p_t)$ zero, at this temperature. Volumetric measurements together with determination of the wavelength of maximum light reflection of these mixtures have shown that their phase transitions Ch/S_A are continuous. Thus the measured volume and enthalpy changes associated with the transitions are pretransitional effects and so we shall denote them as a pretransition volume, $\Delta_t V$, and enthalpy, $\Delta_t H$, in the following (for details see [1]).

From figure 2 we can see that a mixture with $x_{Ch-3} = 0.172$ having $(\partial T_t/\partial p_t) = 0$ at atmospheric pressure (see *b*) exhibits $\Delta_t V$ and $\Delta_t H = 0$ (see *a*). The same must hold true for elevated transition pressures. Kasting *et al.* [2] have verified this for the pressure-induced re-entrant nematic phase behaviour of 4-octyloxy-4′-cyano-biphenyl. Herrmann *et al.* [3] have shown that the pretransition enthalpy of Ch-14 does not disappear before 3000 bar. It seems to be surprising therefore that for some Ch-3/Ch-9/Ch-14 ternary mixtures $\Delta_t H$ and $\Delta_t V$ are already zero at atmospheric pressure. The influence of the component with the shortest *n*-alkyl chain, here Ch-3, on this thermodynamic behaviour is clear: the less Ch-3 is in the mixture, the higher the transition pressure is, where $\Delta_t H$ and $\Delta_t V$ are equal to zero. That follows from figure 1, where the maximum temperature of the Ch/S_A phase boundary is shifted to higher pressure with decreasing mole fraction of Ch-3. This effect should be due to an excess volume generated in the smectic structure by the short Ch-3 molecules, thus relatively enlarging the volume of the smectic phase with respect to that of the cholesteric.
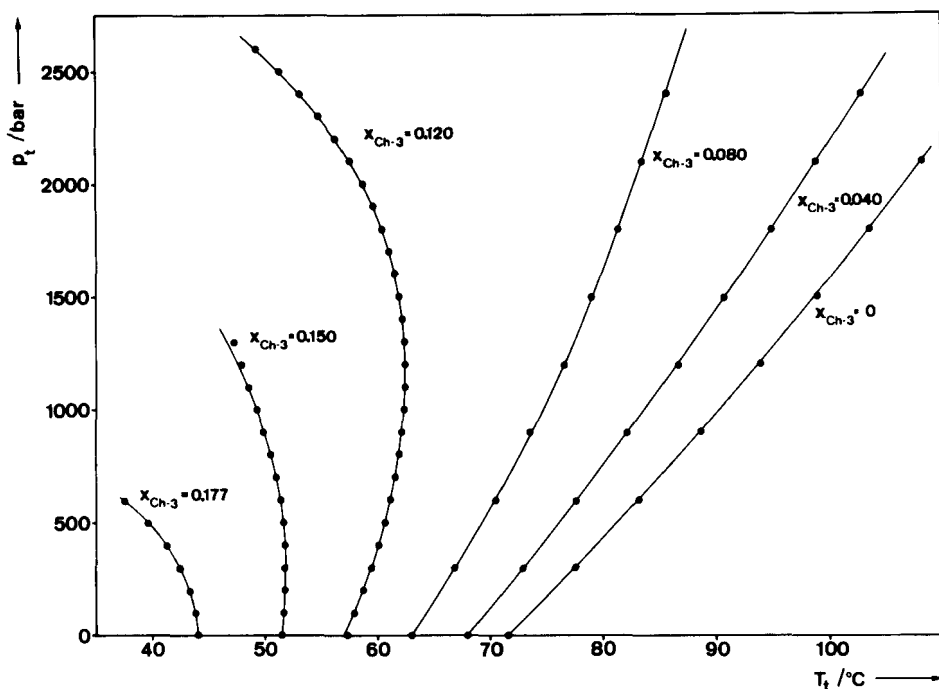
Figure 1. p_t, T_t smectic A–cholesteric phase boundaries of the Ch-3/Ch-9/Ch-14 system; $x_{Ch-9}/x_{Ch-14} = 2\cdot11$.

2. Experimental

The measurements were performed by the same equipment described in the preceding paper [1]. The densimeter had a relative accuracy of 5×10^{-4} per cent. The cholesteryl n-alkanoates were recrystallized repeatedly from acetone/methanol mixtures until the phase transition temperatures were constant and the thin-layer chromatograms uniform.

3. Results

The excess volume ΔV^{ex} which is supposed to occur for a smectic Ch-3/Ch-9/Ch-14 ternary mixture is defined by

$$\Delta V^{ex} = V_t - V_b x_b - V_{Ch-3} x_{Ch-3}, \tag{1}$$

where V_t is the average molar volume of the ternary Ch-3/Ch-9/Ch-14 mixture, V_b is the average molar volume of the binary Ch-9/Ch-14 mixture, V_{Ch-3} is the molar volume of Ch-3, x_b is the mole fraction of the binary Ch-9/Ch-14 mixture, and x_{Ch-3} is the mole fraction of Ch-3. To establish the existence of ΔV^{ex} at various temperatures and mole fractions of Ch-3 we had to determine the dependence of V_t on temperature and the mole fraction of Ch-3 as well as the dependence of V_b and V_{Ch-3} on temperature. ΔV^{ex} was determined from 40–85°C. Since the melting point of Ch-3 is 95·2°C the temperature dependence of V_{Ch-3} in the lower temperature range could only be obtained by an extrapolation procedure. For this purpose the temperature dependence of the cholesteric molar volume of four Ch-3/Ch-9 mixtures was determined between 45 and 90°C. These measurements gave a positive smectic ΔV^{ex}, which seems to be independent of
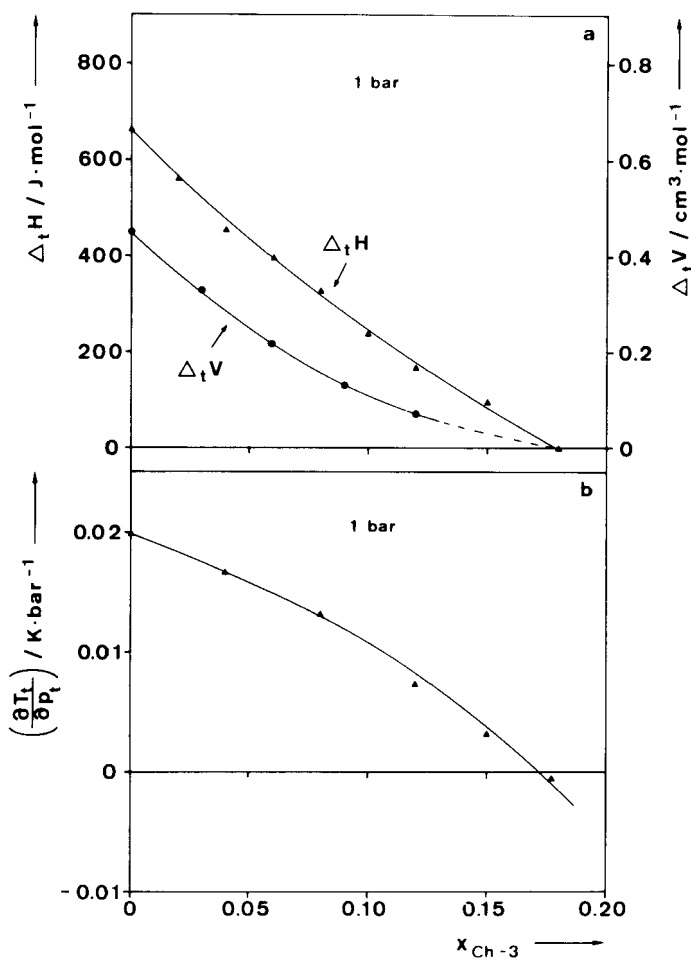
Figure 2. (*a*) Pretransition enthalpy, $\Delta_t H$, and volume, $\Delta_t V$, of the smectic A–cholesteric phase transition and (*b*) slope of the smectic A–cholesteric phase boundary, $(\partial T_t / \partial p_t)$, of the Ch-3/Ch-9/Ch-14 system at atmospheric pressure versus mole fraction, x_{Ch-3}; $x_{Ch-9}/x_{Ch-14} = 2\cdot11$.

temperature within the experimental accuracy. This is shown in figure 3 for six different ternary Ch-3/Ch-9/Ch-14 mixtures. Due to the strong pretransitional effect in the cholesteric phase (smectic-like clusters) ΔV^{ex} disappears only at some distance above the smectic A–cholesteric transition temperature (not shown in figure 3).

In order to demonstrate more precisely the influence of the component with the shortest *n*-alkyl chain on the excess volume in the smectic A phase, ΔV^{ex} is plotted against x_{Ch-3} for $T = 44°C$ in figure 4 (*a*). The solid curve in figure 4 (*a*) was computed by the least squares method. ΔV^{ex} increases with x_{Ch-3} and reaches its highest value at that x_{Ch-3} ($\approx 0\cdot180$), where the S_A phase transforms into the cholesteric. By extrapolating the solid curve to $x_{Ch-3} = 0$ a value of $-0\cdot005\,\text{cm}^3\,\text{mol}^{-1}$ is obtained which indicates that the determination of ΔV^{ex} is correct.

Assuming that no excess volume originates when cholesteric phases without smectic-like clusters are mixed a correlation between the pretransition volume, $\Delta_t V$, and the excess volume, ΔV^{ex}, can be provided which offers another possibility for
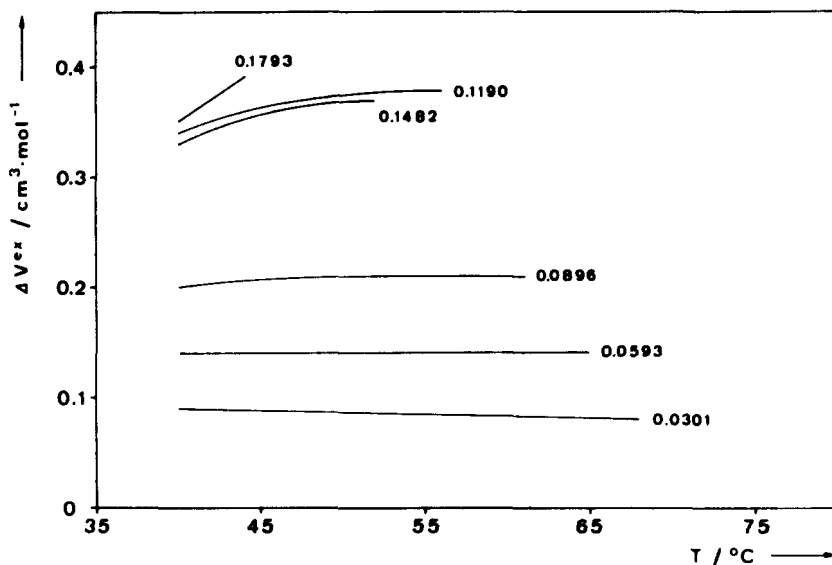
Figure 3. Excess volume, ΔV^{ex}, of the smectic A phase of the Ch-3/Ch-9/Ch-14 system at atmospheric pressure versus temperature, T; $x_{\mathrm{Ch-9}}/x_{\mathrm{Ch-14}} = 2\cdot11$ ($x_{\mathrm{Ch-3}}$ is given on the curves).

determining ΔV^{ex}. This correlation is established in figure 5. A binary cholesteric mixture without smectic-like clusters (a) at 85°C (A) can be transformed into a ternary smectic mixture (b) at 40°C (D) in two different ways. In the first way Ch-3 with $x_{\mathrm{Ch3}} < 0\cdot18$ ($\Delta_t V > 0$; see figure 2(a)) is added to the binary cholesteric mixture (A → B), and then the ternary mixture obtained is cooled from 85 to 40°C into the smectic A phase (B → D). In the second way the binary cholesteric mixture is cooled into the smectic A phase (A → F), and then Ch-3 is added to this mixture with the same mole fraction as for the first method (F → D). In the first method the possible experimental procedure B to D is now replaced by B via C to D, where the ternary cholesteric mixture (b) is hypothetically cooled to C and then transformed into a smectic in D. In the second method for the binary cholesteric mixture (a) A to F is analogously replaced by A via E to F. Now we assume that the volume discontinuities associated with the transformation of the hypothetical cholesteric phases in E and C into the smectic A phases in F and D, respectively, equals the measurable pretransition volumes, $\Delta_t V_0$ and $\Delta_t V_{x_{\mathrm{Ch-3}}}$, of the binary mixture (a) and of the ternary one (b), respectively (cf. figure 5). Equating the volumes in D obtained on both ways (cf. figure 5, lower part), then we obtain a relationship between the excess volume in the smectic A phase, ΔV^{ex}, and the pretransition volume, $\Delta_t V_{x_{\mathrm{Ch-3}}}$:

$$\Delta V^{\mathrm{ex}} = \Delta_t V_0 (1 - x_{\mathrm{Ch-3}}) - \Delta_t V_{x_{\mathrm{Ch-3}}}, \qquad (2)$$

where $1 - \chi_{\mathrm{Ch-3}}$ is χ_{b}. According to equation (2) ΔV^{ex} is independent on temperature. This is in agreement with the results of the measurement in figure 3. Equation (2) was then employed to calculate ΔV^{ex} as a function of $x_{\mathrm{Ch-3}}$ by means of the $\Delta_t V_{x_{\mathrm{Ch-3}}}$ values given in figure 2. The resulting dashed curve in figure 4 (a) (b) shows the curve for the total $x_{\mathrm{Ch-3}}$ range) agrees well with the solid line based on quite different measurements, described previously. This satisfactory agreement of both curves supports the
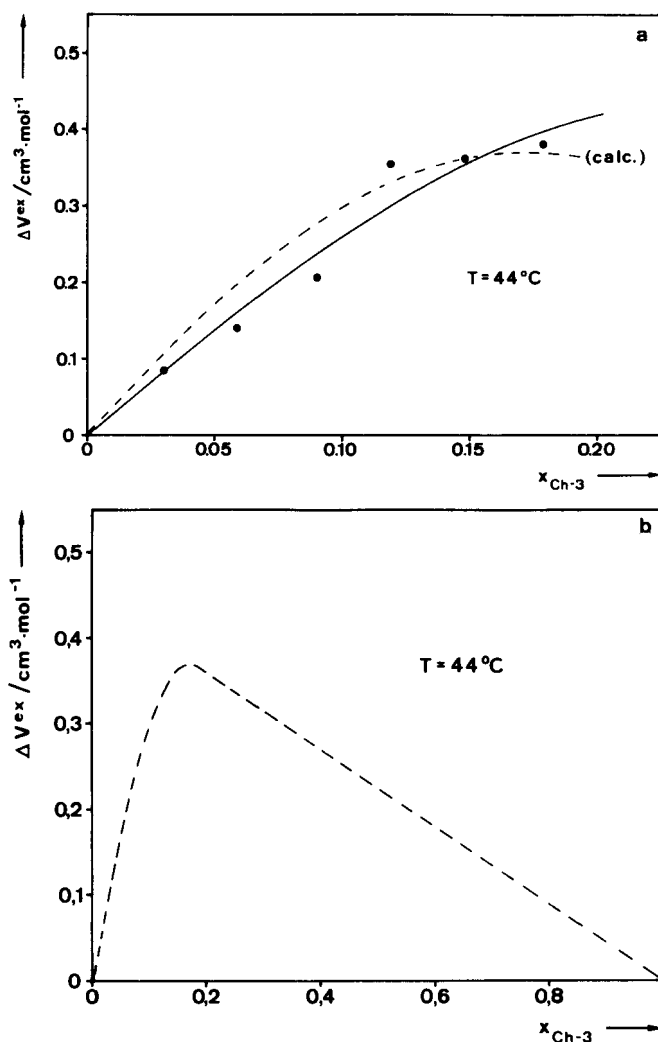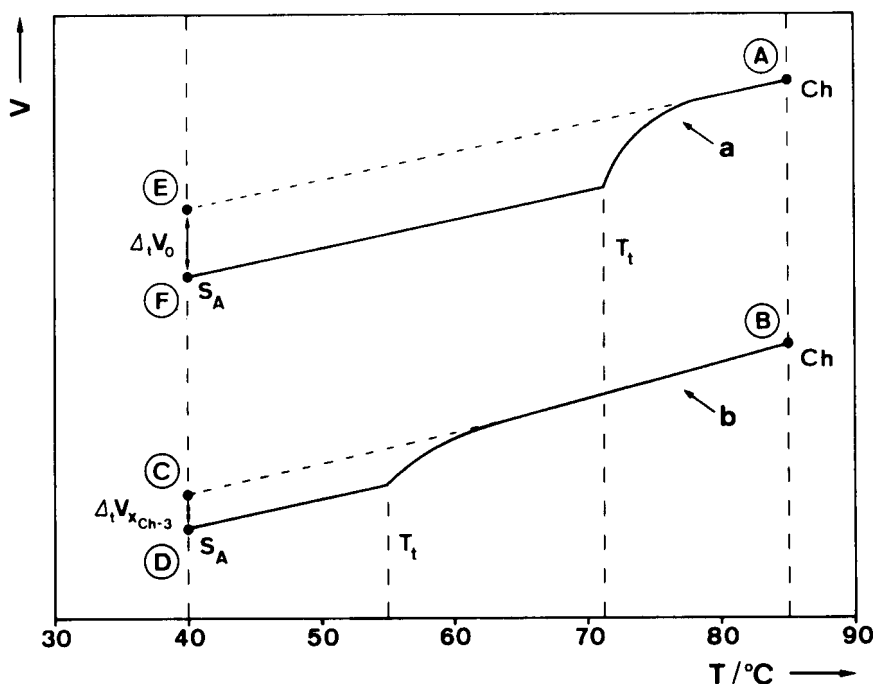
Figure 4.   Excess volume, ΔV^{ex}, of the Ch-3/Ch-9/Ch-14 system at atmospheric pressure and
$T = 44°C$ versus mole fraction, x_{Ch-3}; $x_{Ch-9}/x_{Ch-14} = 2·11$. ($a$) Solid curve: computed by
the least squares method on the basis of the values according to equation (1) (circles);
dashed curve: computed on the basis of the values according to (equation (2)). (b) dashed
curve: computed as in (a) here for the total x_{Ch-3} range.

reliability of the ΔV^{ex} values. The dashed line in figure 2 reveals a maximum value at
about that x_{Ch-3} (0·180), where $\Delta_t V$ in figure 2 approaches zero. This maximum ΔV^{ex},
of approximately 0·40 cm³ mol⁻¹, compensates the residual $\Delta_t V_0 x_b$ of 0·37 cm³ mol⁻¹
($x_b = 0·820$) attributed to the components Ch-9 and Ch-14 (cf. figure 2 ($x_{Ch-3} = 0$):
$\Delta_t V_0 = 0·45$ cm³ mol⁻¹). This compensation condition $\Delta V^{ex} = \Delta_t V_0 x_b$ is valid for all
ternary mixtures with $x_{Ch-3} > 0·180$. Consequently the extraordinary phase behaviour
of the Ch-3/Ch-9/Ch-14 mixtures described earlier is attributed to a positive excess
volume caused by Ch-3, which has a considerably shorter n-alkyl chain than the other
two components. Replacing Ch-3 by a component with a shorter or a longer n-alkyl

Figure 5.   Schematic representation of the temperature dependence of the molar volume, V, of a binary Ch-9/Ch-14 (a) and a ternary Ch-3/Ch-9/Ch-14 mixture (b); $\Delta_t V_0$ and $\Delta_t V_{x_{Ch-3}}$ are the respective Ch/S$_A$ pretransition volumes. $x_{Ch-9}/x_{Ch-14} = 2 \cdot 11$ ($V_{b,T}$: average molar volume of the binary mixture, $V_{Ch-3,T}$: molar volume of Ch-3 at temperature T).

chain the observed effects on the thermodynamic behaviour of the ternary mixtures should be enhanced or weakened. In order to examine the latter considerations the Ch/S$_A$ phase boundaries of the ternary systems Ch-1 (cholesteryl formate)/Ch-9/Ch-14 on the one hand and Ch-5 (cholesteryl pentanoate)/Ch-9/Ch-14 and Ch-8 (cholesteryl octanoate)/Ch-9/Ch-14 on the other were determined (experimental method see [1]). The phase boundaries are displayed in figures 6–8.

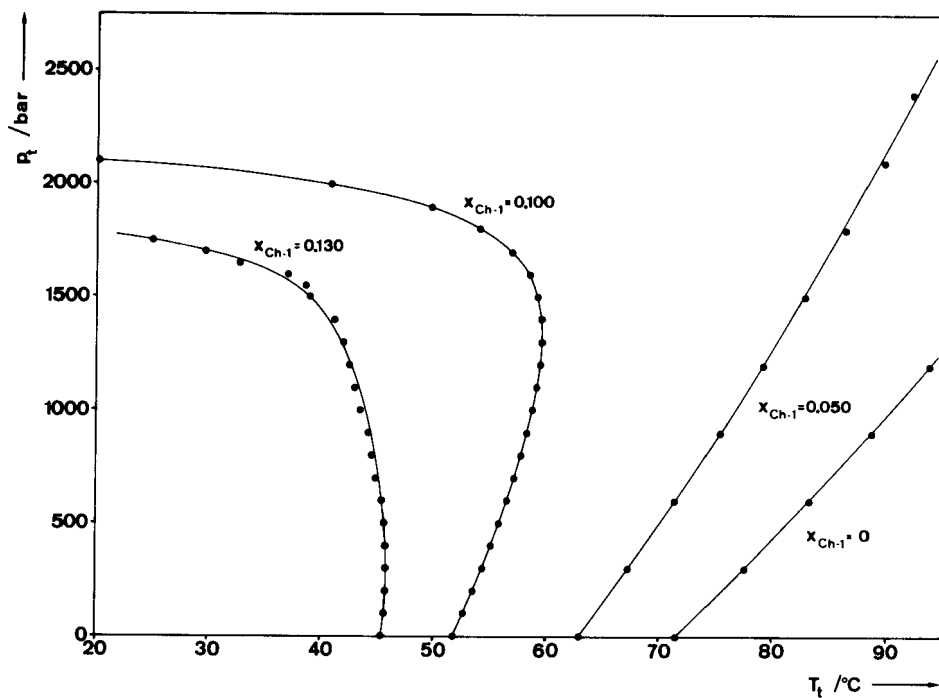Figure 6. p_t, T_t smectic A–cholesteric phase boundaries of the Ch-1/Ch-9/Ch-14 system; $x_{Ch-9}/x_{Ch-14} = 2.11$.
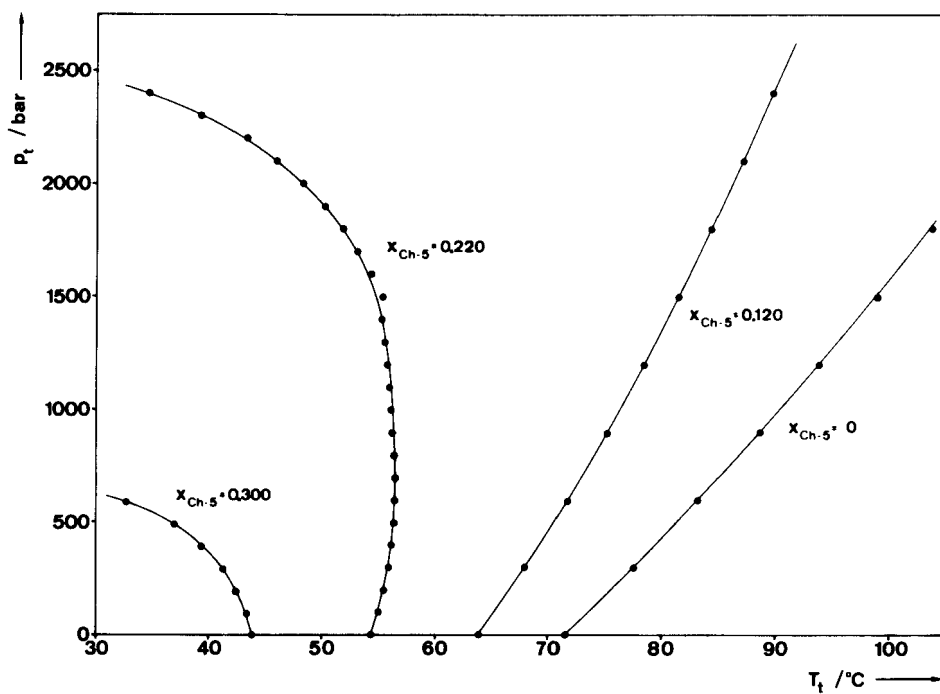

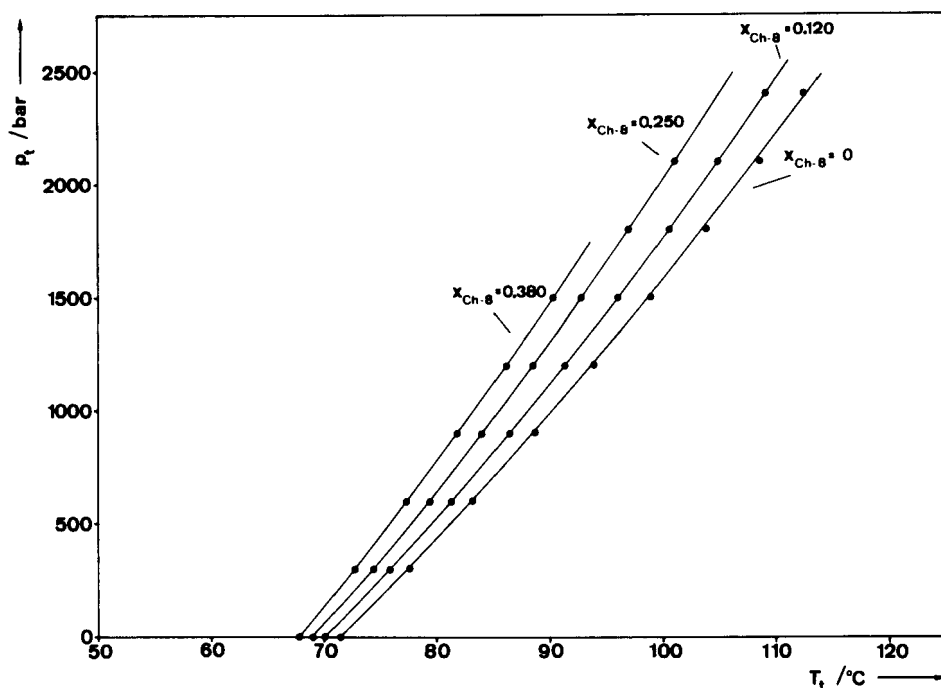Figure 7. p_t, T_t smectic A–cholesteric phase boundaries of the Ch-5/Ch-9/Ch-14 system; $x_{Ch-9}/x_{Ch-14} = 2 \cdot 11$.

Figure 8. p_t, T_t smectic A–cholesteric phase boundaries of the Ch-8/Ch-9/Ch-14 system;
$x_{\text{Ch-9}}/x_{\text{Ch-14}} = 2\cdot11$.

Calorimetric investigations on these systems at atmospheric pressure show, with one exception, an analogous result as for the Ch-3/Ch-9/Ch-14: $\Delta_t H$ is equal to zero at about that mole fraction of Ch-1 and Ch-5, where $(\partial T_t)/\partial p_t)_{1\,\text{bar}}$ is also equal to zero (cf. figure 9). This relation could not be observed for the Ch-8/Ch-9/Ch-14 system. In order to demonstrate the influence of the n-alkyl chain length on this thermo-dynamic behaviour, in figure 10 the pressure coordinate of the maximum of tem-perature of the Ch/S_A phase boundaries, $p_t((\partial T_t/\partial p_t) = 0; (\partial p_t/\partial T_t) = \infty$, respective-ly), is plotted versus the mole fraction of the component with the shortest n-alkyl chain of the ternary mixture concerned, x. The higher x the lower p_t is, where $(\partial T_t/\partial p_t)$ and also $\Delta_t V$ and $\Delta_t H$ are equal to zero. The shorter the n-alkyl chain, the lower the value of x needed to achieve the same p_t with $(\partial T_t/\partial p_t) = 0$. The dependence of this special p_t on x is very strong and seems to be very similar for all three ternary systems.

4.   Discussion

The thermodynamic behaviour of ternary mixtures of the cholesteryl n-alkanoates investigated can be understood by means of figure 11. Here, the smectic A–cholesteric transition temperature, T_t, of the mixtures is plotted versus the mole fraction, x, of the component with the shortest n-alkyl chain. Except for Ch-8, these chains are so short that all other compounds do not themselves form a smectic A phase. Thus, the addition of these compounds to the Ch-9/Ch-14 mixture $(x_{\text{Ch-9}}/x_{\text{Ch-14}} = 2\cdot11)$
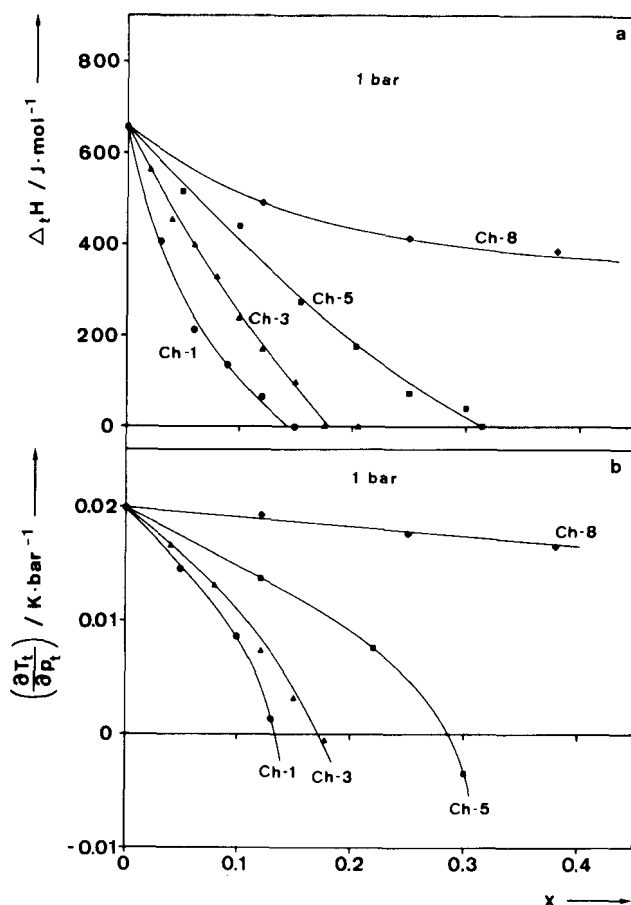
Figure 9. (a) Pretransition enthalpy, $\Delta_t H$, of the smectic A–cholesteric phase transition and (b) slope of the Ch/S_A phase boundaries, $(\partial T_t / \partial p_t)$, of four Ch-$N$/Ch-9/Ch-14 systems ($N = 1, 3, 5, 8$) at atmospheric pressure versus mole fraction, x, of the component with the shortest n-alkyl chain; $x_{Ch-9} / x_{Ch-14} = 2 \cdot 11$.

destabilizes its smectic structure; this is indicated by the increasing depression of T_t with increasing x. Already at about 46°C the smectic A phase becomes metastable. The shorter the n-alkyl chain is the stronger the destabilizing effect. It is quite understandable that Ch-8 exhibits this only to a small degree. The destabilizing influence of the components with the very short n-alkyl chains is also the cause of the extraordinary thermodynamic behaviour of the ternary mixtures (see in particularly figure 10). This influence manifests itself, for instance, in an excess volume as shown before. Since the n-alkyl chains of Ch-1, Ch-3 and Ch-5, are considerably shorter than that of Ch-9 and Ch-14, holes probably originate in the smectic structure through the addition of these components. Due to [4] kinking of the chains Ch-9 and Ch-14 can be excluded in this connection; both cholesteryl n-alkanoates are fully extented in the liquid-crystalline state.

In conclusion the pressure-induced re-entrant cholesteric (Ch_{re}) phase behaviour is explained by the example of the ternary mixture with $x_{Ch-3} = 0 \cdot 120$ (cf. figure 1),
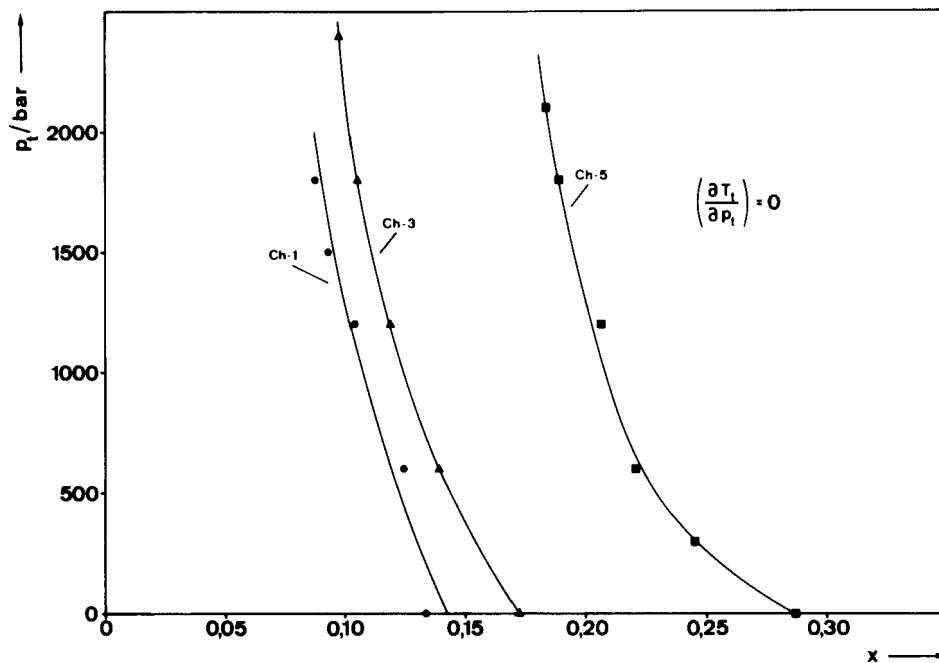
Figure 10. Smectic A–cholesteric phase transition pressure, p_t, where the slope of the phase boundaries, $(\partial T_t / \partial p_t)$, is equal to zero, versus mole fraction, x, of the component with the shortest n-alkyl chain of three Ch-N/Ch-9/Ch-14 systems ($N = 1, 3, 5$); $x_{Ch-9}/x_{Ch-14} = 2\cdot11$.

which has the phase sequence

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

at $T_t = 60°C$. In [1] it has been shown that the difference of the compressibility factors $\Delta\kappa(=\kappa(Ch) - \kappa(S_A))$ for both phase transitions is positive. This means that at 1855 bar looking with increasing pressure a transition into a phase occurs which exhibits the higher compressibility. This is opposite to what is usually found; what can be the reason for it? Since ΔV^{ex} decreases following the Ch/S_A phase boundary upwards (from 1200 bar onwards $\Delta_t V_{x_{Ch-3}} = 0$, so $\Delta V^{ex} = \Delta_t V_0 x_b$, which decreases with pressure [5]), it should also decrease between 395 and 1855 bar, when the pressure is increased isothermally. At lower pressure the compressibility parallel to the planes of the smectic layers should predominate so that the smectic A phase is stabilized. At higher pressure the compressibility perpendicular to the planes then should destabilize the S_A phase: the molecules are increasingly forced into the holes, which reduces ΔV^{ex}. At 1855 bar finally the layer structure is destroyed and the S_A phase transforms into the Ch_{re} phase. At this relatively low transition pressure $\Delta_t V_0$ is still non-zero [5] and thus ΔV^{ex}, too. The excess volume of the cholesteric phase is contained in smectic-like clusters, which have a cholesteric environment. ΔV^{ex}, therefore, should decrease with pressure at a faster rate than in the smectic A phase.
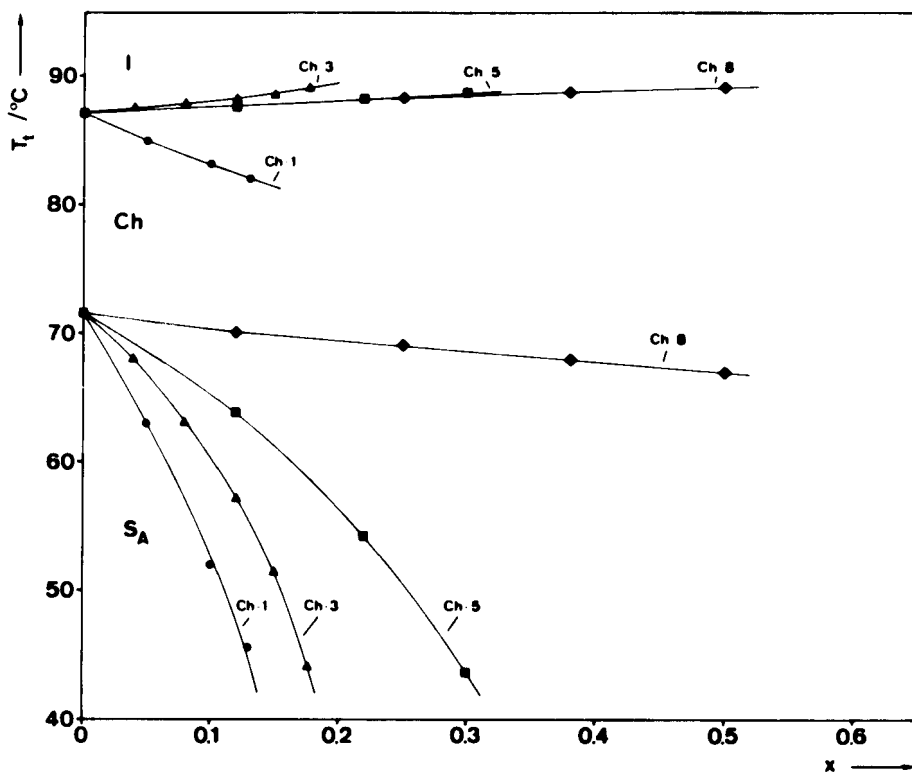
Figure 11. Smectic A–cholesteric and cholesteric–isotropic transition temperature, T_t, of four Ch-N/Ch-9/Ch-14 systems (N = 1, 3, 5, 8) at atmospheric pressure versus mole fraction, x, of the component with the shortest n-alkyl chain; x_{Ch-9}/x_{Ch-14} = 2·11.

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