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Preliminary communication

Interdependence of liquid crystal phase transitions in mixed systems

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From calorimetric measurements, the phase transition enthalpies and entropies in mixed systems of each of two cholesteryl esters with a nematogenic compound PCPB have been determined as a function of composition. The calorimetric data for the LC–I transition, as well as the slope $(\mathrm{d}p/\mathrm{d}T)_t$ of the phase boundary line LC–I, show a conspicuous discontinuity at the critical mole fraction of PCPB where the blue phases disappear. The enthalpy of the SmA–N* transition becomes zero at the same critical mole fraction. Possible reasons for the observed transition interdependence are discussed.

There are only few examples in the literature showing that there may be an interdependence of different phase transitions in liquid crystalline systems. By their high pressure investigations of phase diagrams of liquid crystalline mixtures, Shashidhar *et al.* [1] have found a marked anomaly in the slope of the N–I phase boundary line (at atmospheric pressure) just at those mole fractions where the re-entrant nematic phase appears and disappears. Pollmann and Voß [2] have shown a correlation between the pretransitional behaviour of the optical activity in the isotropic liquid phase and the phase behaviour of blue phases (BPs) at high pressures. In a chiral/racemic mixed system, Slaney and Goodby [3] observed that the BPs break down just at those concentrations where the TGBA phases disappear. In this paper we present a further but still more complex example for the interdependence of liquid crystal phase transitions.

Two binary mixtures have been investigated: cholesteryl nonanoate (CH9) and cholesteryl tetradecanoate (CH14) were each mixed with *p*-pentylphenyl-2-chloro-4-(*p*-pentylbenzoyloxy)benzoate (PCPB). The cholesteryl esters exhibit the phase sequences Cr–SmA–N*–BPI–BPII–BPIII–I and PCPB has the sequence Cr–N–I. For comparison, the experimental data measured for the phase transitions from the liquid crystalline phases (LC) to the isotropic liquid in both mixed systems are collected in figure 1 and plotted vs. the mole fraction x of PCPB.

We have determined the pressure/temperature phase diagrams for different mixtures by means of high pressure experiments [4]. In figure 1 (*a*) the slope $(\mathrm{d}p/\mathrm{d}T)_t$ of the LC–I phase boundary line at atmospheric pressure is given vs. x(PCPB). The subscript ‘t’ here and in the following text indicates that the data are measured at the phase transitions under discussion. To obtain these data, the pressure dependence of the clearing temperature T_c must be known; this was determined by light reflection measurements [4]. A striking discontinuity in $(\mathrm{d}p/\mathrm{d}T)_t$ at about $x = 0.65$ for both systems is obvious. By microscopic observations it could be shown that above the discontinuity point (for CH9/PCPB, $x > 0.64$; for CH14/PCPB, $x > 0.66$) the formation of BPs no longer occurs and the cholesteric phase now transforms directly into the isotropic liquid.

In figure 1 (*b*) the phase transition enthalpy $\Delta_t H$ for the N*–I transition (obtained by DSC-2 measurements [5]) is given; the value includes the small BP enthalpy effects in the regions $x < 0.64$ (CH9/PCPB) and $x < 0.66$ (CH14/PCPB). Again a clear discontinuity occurs in the curves $\Delta_t H(x)$ just at the same mole fractions as in figure 1 (*a*). The dependence of $\Delta_t H$ on x(PCPB) in the BP part of the mixed systems is rather small, but increases in the higher x range where BPs no longer exist.

The wavelength of maximum light reflection λ_t of the cholesteric phase which is proportional to the helical pitch is given in figure 1 (*c*) vs. x(PCPB) showing a monotonic increase with x. Above the critical λ_t values of 575 nm (CH9/PCPB) and 570 nm (CH14/PCPB), the

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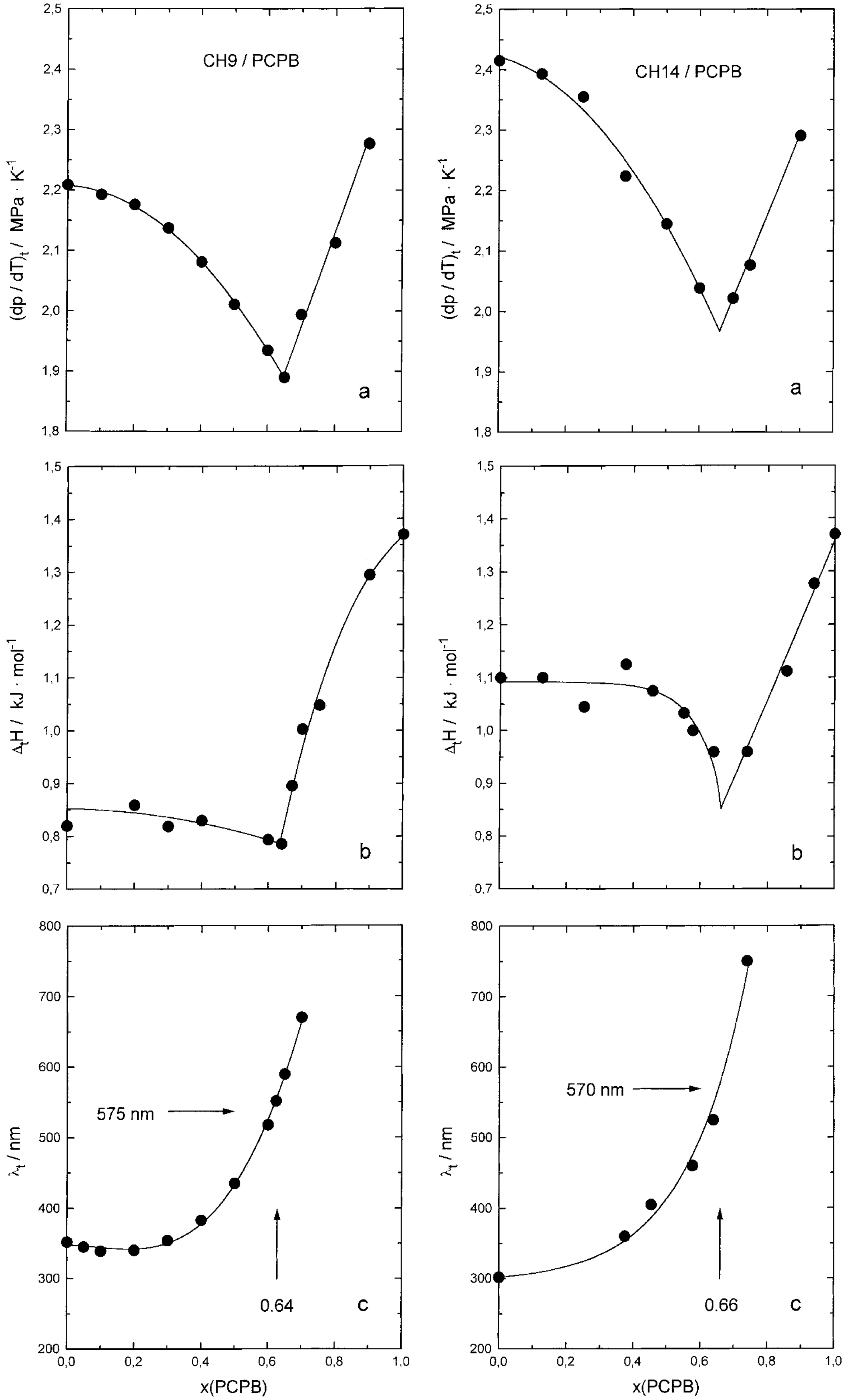

Figure 1. Phase transition data for the systems CH9/PCPB (left hand) and CH14/PCPB (right hand) vs. mole fraction x of PCPB. (*a*) Slope $(\mathrm{d}p/\mathrm{d}T)_t$ of the phase boundary line (at atmospheric pressure) for the transitions BP–I and N*–I, respectively; (*b*) N*–I transition enthalpy $\Delta_t H$, including all enthalpy effects of transitions where BPs are involved; (*c*) wavelength of maximum light reflection λ_t of the cholesteric phase at the N*–BP and N*–I phase transition points, respectively.

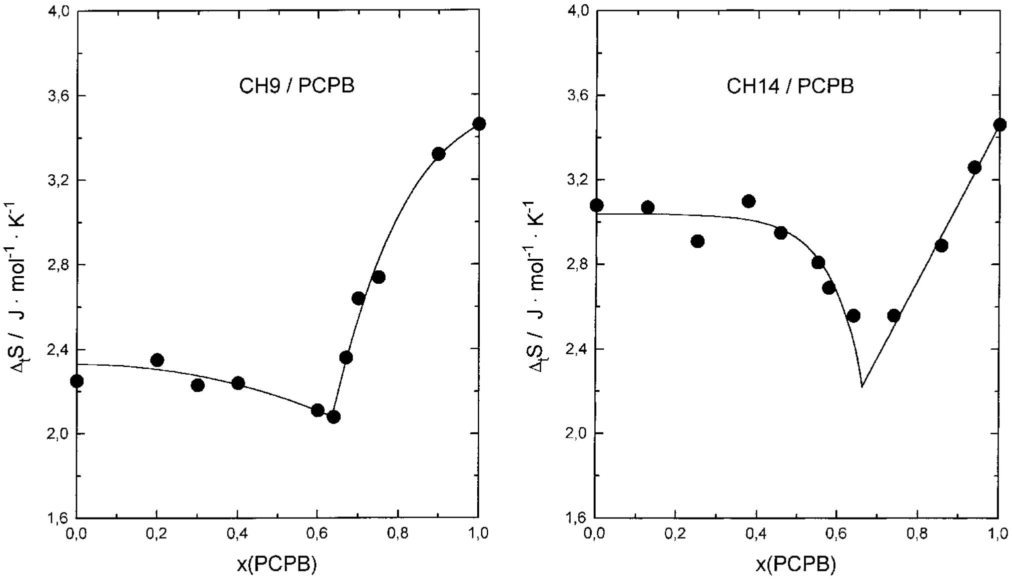

Figure 2. N*–I transition entropy $\Delta_t S$ in the systems CH9/PCPB (left hand) and CH14/PCPB (right hand) including all entropy effects of transitions where BPs are involved vs. mole fraction x of PCPB.

BPs are no longer stable. It is well known from earlier experiments that chiral LC systems with larger pitches (i.e. low chirality) do not exhibit BPs [6]. This effect can also be understood from theoretical considerations [7]. However, it turns out that there is no discontinuity in the curves $\lambda_t(x)$ at the mole fractions of PCPB where the BPs disappear.

Since the clearing temperature T_c of the systems has been measured and found to increase in a monotonic way with x(PCPB), the corresponding phase transition entropies $\Delta_t S = \Delta_t H/T_c$ could be evaluated. As shown in figure 2 for the two systems, the dependence of $\Delta_t S$ on x(PCPB) is analogous to that of the transition enthalpies, also with a conspicuous discontinuity.

The transition of the smectic A phase to the cholesteric phase in the system CH14/PCPB reveals a thermodynamical peculiarity as well. As shown in figure 3 the enthalpy $\Delta_t H$ for this transition decreases steeply with x(PCPB) [5]. It should be stressed that PCPB itself does not possess a SmA phase. The strong decrease of the SmA–N* transition temperature with x(PCPB) also indicates a destabilization of the SmA phase in this system. It could be verified by polarizing microscopy that the SmA phase up to $x = 0.558$ still exists. At higher mole fractions crystallization could no longer be suppressed. The SmA–N* transition changes from enantiotropic to monotropic behaviour at $x(\text{PCPB}) \approx 0.4$. The experimental curve $\Delta_t H(x)$ can easily be extrapolated to zero at $x(\text{PCPB}) = 0.66$. This is just the mole fraction in the C14/PCPB system where the clearing enthalpy and the value of $(\mathrm{d}p/\mathrm{d}T)_t$ of the N*–BP and N*–I transition, respectively, show a conspicuous discontinuity, cf. figures 1(*a*) and 1(*b*). In other words in the regions where the BPs are no longer stable, the SmA–N* transition enthalpy is zero.

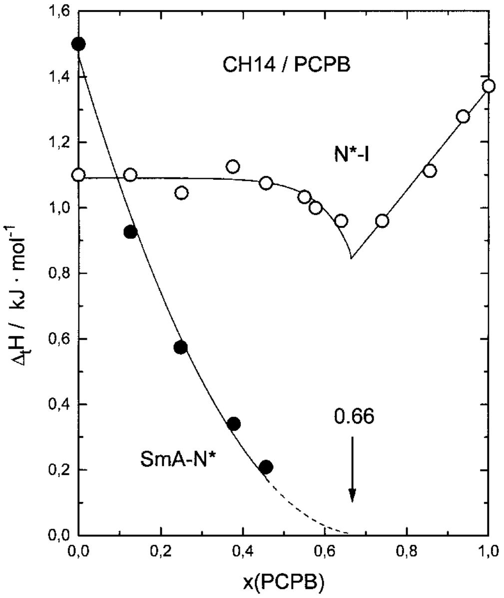

Figure 3. The enthalpy $\Delta_t H$ of the SmA–N* transition in the system CH14/PCPB vs. mole fraction x of PCPB. For comparison, the clearing enthalpy $\Delta_t H$ taken from figure 1(*b*) is given above.

A diagram analogous to figure 3 could not be obtained for the system CH9/PCPB. $\Delta_t H$ could not be measured at x(PCPB) > 0.4 because it is essentially smaller than that of CH14. The result given in figure 3 does not seem to be fortuitous. It is an open question whether there is any relation between the tendencies in chiral LC systems to form BPs and a SmA phase, but our results give a hint in support of it. In this connection we mention a comparable situation in systems with TGB phases. The formation of TGB phases obviously is governed by two cooperating factors: the chirality of the system and its tendency to create smectic layers [8, 9].

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