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INVESTIGATIONS OF PHASE DIAGRAMS WITH MONOTROPIC LIQUID-CRYSTALLINE PHASES

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ABSTRACT

The phase transitions in two eutectic liquid-crystalline systems with monotropic behaviour have been investigated by differential scanning calorimetry (DSC). The monotropic phase transition becomes enantiotropic as a function of composition, because a phase equilibrium line intersects with one liquidus line. Consequently, a horizontal phase equilibrium line occurs which separates two two-phase regions. The special features of these complicated phase diagrams are discussed and experimentally verified.

INTRODUCTION

Several thousands of organic compounds are now known to form liquid crystals. An essential requirement for mesomorphism to occur is that the molecule must be geometrically highly anisotropic. In the crystalline state those molecules exhibit a high degree of long-range orientational order additionally to their long-range translational order. At the melting temperature, molecules of very anisotropic shape tend to maintain a parallel orientation even though they are free to diffuse in a manner typical of fluids (Fig. 1). When only this orientational order is present, the phase is called a *nematic* liquid crystal, shown in Fig. 2a. In some cases, one- or two -dimension positional order is preserved after melting together with the orientational order. This is the case in *smectic* phases given in Fig. 2b. Chiral molecules form a phase in which the direction of preferred orientation rotates about a helical axis. This phase is called the *cholesteric* phase shown in Fig. 2c. Many mesomorphic substances exhibit a polymorphism with different liquid crystalline phases existing between the solid and isotropic state.

In a considerable number of mesogenic organic compounds, the liquid-crystalline phases are *monotropic*, i. e. they will be formed only on cooling below the melting point by spontaneous organization from the supercooled melt. For technical applications usually *eutectic* mixed systems of mesogenic compounds are used with the eutectic composition, due to their wide mesomorphic range. For this reason, a large number of phase diagrams of mixed systems exhibiting mesophases

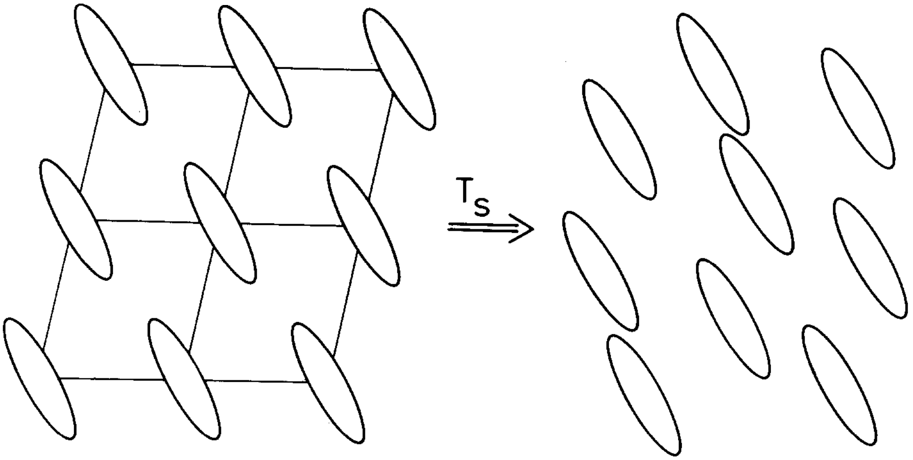

Fig. 1 Schematic representation of the phase transition crystalline → liquid-crystalline (T_S : melting temperature).

have been studied (ref. 1). Many of these mixed systems show simple eutectic behaviour. Sometimes, however, an enantiotropic transition into a mesophase becomes monotropic (or vice versa) as a function of composition. In binary mixed systems in which an enantiotropic transition changes into a monotropic one, the simple eutectic phase diagram gets more complex. A change from monotropic to enantiotropic in the mixed system results in an intersection of a phase equilibrium line and one of the liquidus lines. By the intersection of the liquidus line consequently the two-phase region splits up into two two-phase regions.

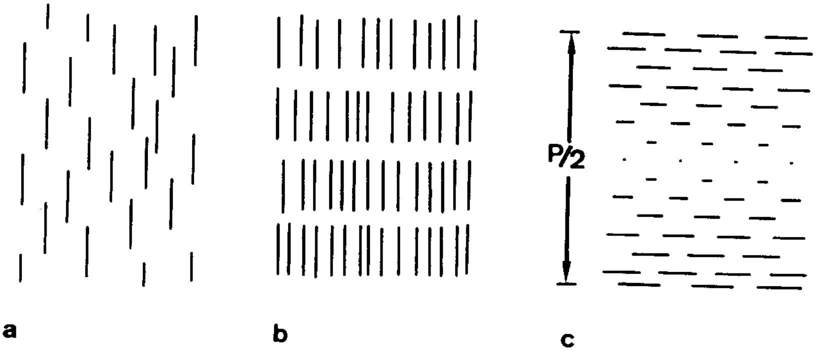

Fig. 2 Different types of liquid crystals:
a) nematic, b) smectic A, c) cholesteric.

Although the appearance of the horizontal phase equilibrium lines between two two-phase regions is absolutely necessary if any phase equilibrium line intersects one of the liquidus lines (ref. 2 - 5), they are missing in many published phase diagrams of binary eutectic mixed systems with such an intersection point (ref. 6 - 16). The reason for this may be the fact that the experimental measurement of this phase equilibrium line is rather difficult. Three problems arise: i) the transition of the melted part of the sample will be superimposed on the melting of the crystalline part; ii) if the composition of the intersection points is far from the eutectic composition, the mass of the melt is small and the thermodynamic effects resulting from the phase transition of the melted part are also small (for example ΔH); iii) the thermodynamic effects of the phase transition meso/meso or meso/iso are themselves small with respect to the melting transition.

EXPERIMENTAL

All substances, cholesteryl acetate (Ch-2), -myristate (Ch-14), -chloride (CC), trans, trans-4'-n-heptyl-bicyclohexyl-4-nitril (CCH 7), E. Merck, and p-pentyl-phenyl-2-chloro-4-(p-pentylbenoyloxy)-benzoate (PCPB), Eastman, were purified by recrystallizing the samples several times in an appropriate solvent.

The phase transition temperatures were obtained by DSC investigations (DSC-2, Perkin-Elmer) and additionally by polarization microscopy (Leitz Ortholux II - POL BK with Mettler heating stage FP 5/52).

RESULTS

Two different mixed systems with intersection points between a liquidus line and a phase equilibrium line were investigated. Because of the described difficulties, we looked specifically for the horizontal phase equilibrium lines between the different two-phase regions. In the case that the two-phase region cryst/meso goes into the region cryst/iso, the investigation of the transition is possible by means of the polarizing microscope. Heating up a mixture with such a phase transition, we can see at T_E the start of the melt. Between crossed polarizers the crystalline and mesogenic parts are both coloured. At the phase transition cryst/meso → cryst/iso, the mesogenic part goes into the isotropic liquid. Above the phase transition, there are coloured crystals embedded in the black isotropic liquid. Heating up, more and more crystals melt and above the liquidus line the whole field of view is black. Fig. 3 shows a mixed system possessing such behaviour. The phase transition cryst/meso → cryst/iso can also be seen in the DSC thermograms. In Fig. 4 there are two DSC traces of the system CC/CCH 7 (ref. 17). In sample A the cholesteric mesophase is enantiotropic. The thermogram shows the eutectic peak, the melting peak, and the iso-

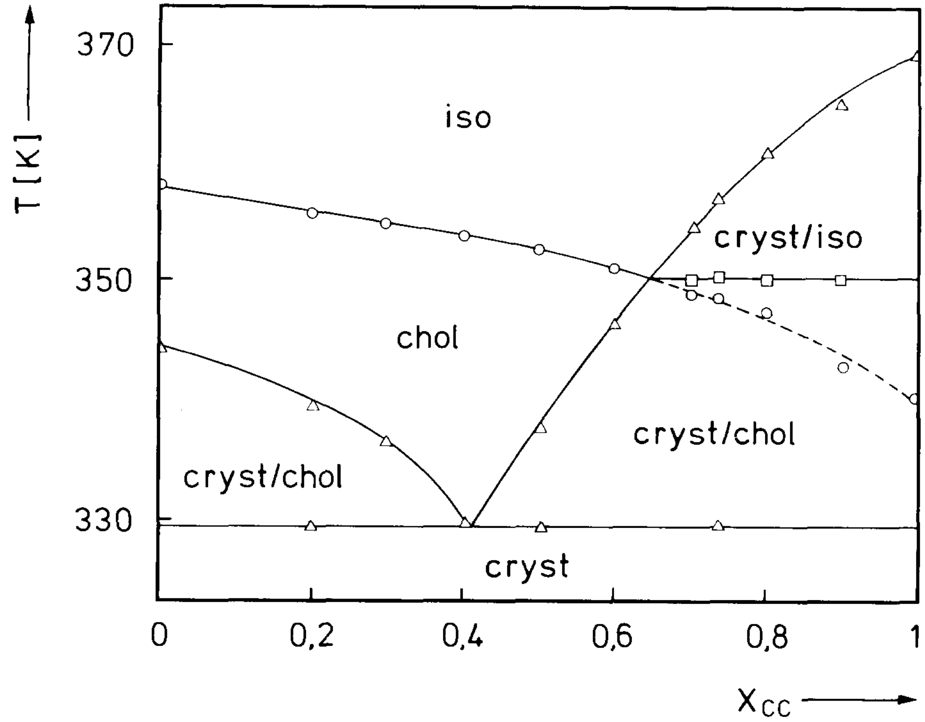

Fig. 3 Phase diagram of the mixed system CCH 7/CC. Two-phase region chol/iso is omitted.

tropic peak. The mixture B has only a monotropic cholesteric mesophase. When the crystalline mixture is heated, first the eutectic composition melts. Further temperature elevation causes more and more CC to melt, until at 350 K the liquidus line intersects the equilibrium line chol/iso. At that temperature the cholesteric part transforms into the isotropic liquid resulting in an additional sharp transition peak. At higher temperature the last crystalline part becomes isotropic.

Fig. 5 shows a phase diagram where the equilibrium line smectic-A/cholesteric intersects a liquidus line. In such a case the determination of the transition cryst/chol → cryst/S_A ist very difficult by means of polarization microscopy. In Fig. 6 two DSC thermograms of different mixtures of the system Ch-14/PCPB are given. Mixture A has an enantiotropic smectic A and an enantiotropic cholesteric phase. Heating up such a mixture, first the eutectic composition melts into the cholesteric state at 308 K. Further temperature elevation turns more and more crystalline Ch-14 into the cholesteric state. At 337 K the equilibrium line smectic-A/cholesteric intersects the liquidus line. The cholesteric

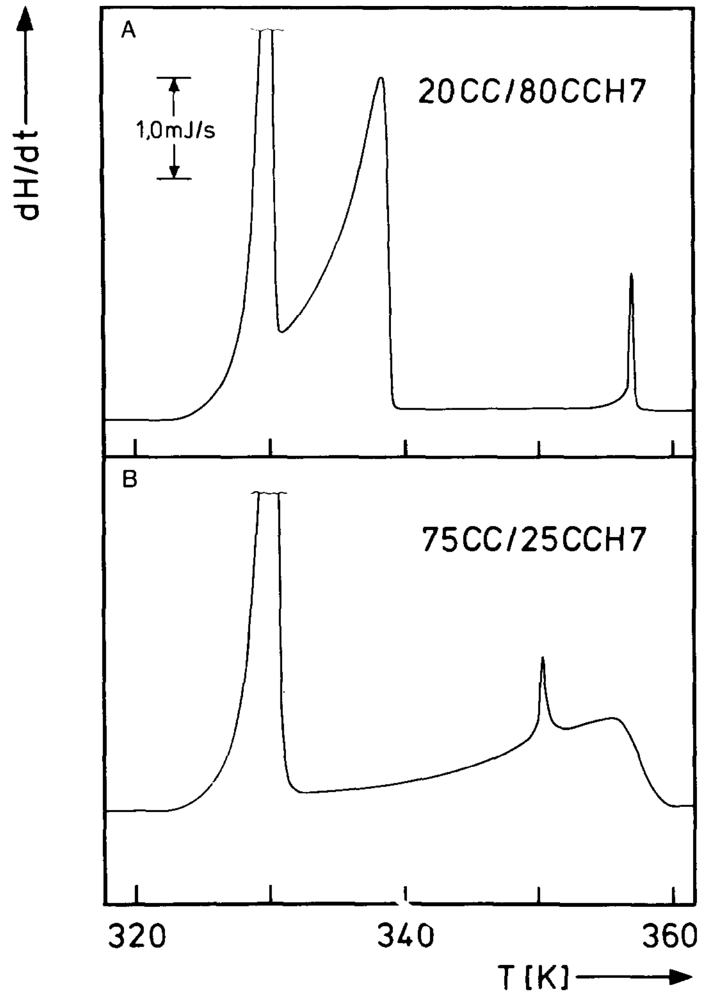

Fig. 4 DSC-traces of two different compositions of the system CCH 7/CC. Sample mass ca. 5.5 mg, heating rate 5 K/min.

part of the sample transforms into the smectic A phase. In the DSC trace we see a shoulder in the melting peak. At the liquidus line the whole sample is in the smectic A state. Further heating brings the sample into the cholesteric phase and finally into the isotropic liquid. Sample B is a mixture with only one enantiotropic cholesteric mesophase. At 308 K the eutectic composition goes into the cholesteric state. Heating up, more and more Ch-14 becomes cholesteric. At 364 K the sample goes into the isotropic liquid. The small transition peaks close below the isotropic transition show the transition cholesteric → Blue

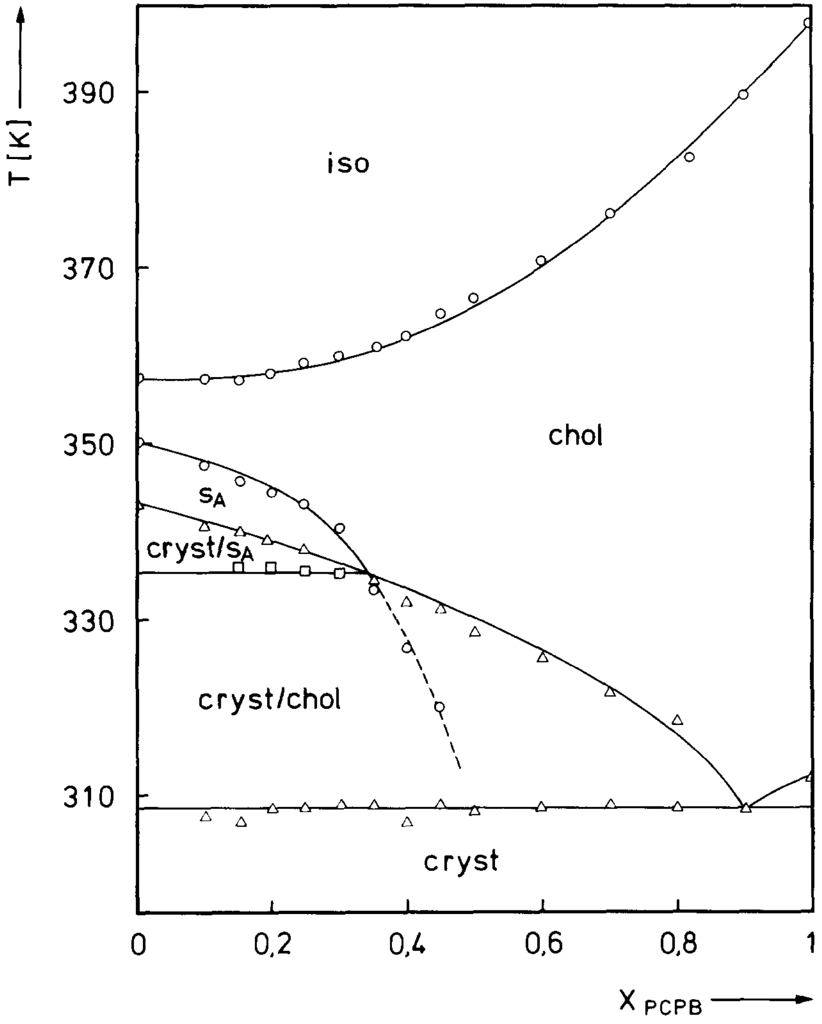

Fig. 5 Phase diagram of the mixed system Ch-14/PCPB. Two-phase regions chol/iso and S_A/chol are omitted.

Phase (ref. 18). As the temperature range of the Blue Phases is very small (≈0.5 K), we do not show the Blue Phase region in Fig. 5.

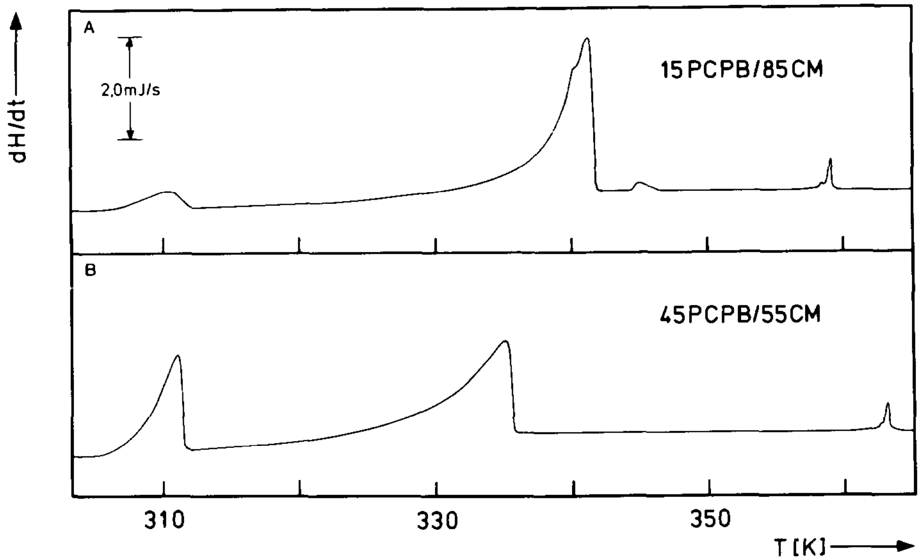

Fig. 6 DSC-traces of two different compositions of the system Ch-14/PCPB. Sample mass ca. 10 mg, heating rate 1.25 K/min.

CONCLUDING REMARKS

In all mixed systems in which an enantiotropic transition changes into a monotropic one by composition variation (or vice versa), the two-phase region between the solidus line and the liquidus line splits up into two two-phase regions with a horizontal phase equilibrium line. These equilibrium lines can be determined by polarization microscopy or DSC investigations. In the melted part of the two-phase regions below the liquidus line in systems with more than one liquid crystalline phase, the phase sequence is reversed (cf. Fig. 5). Such an effect must not be confused with the reentrant behaviour observed in liquid-crystalline mixed systems (ref. 19), where the phase transition sequence of homogeneous phases is reserved. The phase sequence reported here is only a composition effect within the melted part of the two-phase regions.

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