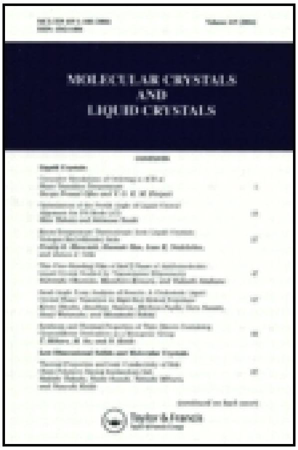

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PHASE DIAGRAMS OF EUTECTIC MIXED SYSTEMS WITH MONOTROPIC LIQUID-CRYSTALLINE PHASES

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The phase diagrams of three different eutectic liquid-crystalline systems with monotropic transitions have been investigated by differential scanning calorimetry (DSC) as well as by polarization microscopy. In all systems the monotropic transition becomes enantiotropic as a function of composition, because of the intersection of a phase equilibrium line 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.

In the case of systems with more than one mesomorphic phase, the high temperature mesophase again appears in the low temperature two-phase region. This effect may simulate a reentrant behaviour of liquid crystalline systems.

1. INTRODUCTION

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 have been studied[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. The phase diagrams resulting in these cases are rather complicated. It is the aim of this paper to point out the special features of those phase diagrams which sometimes have been overlooked in the literature.

2. GENERAL REMARKS

It is well known that a two-component solid-liquid equilibrium with liquids miscible in all properties and no appreciable solid-solid solubility, gives a simple eutectic phase-diagram (for example Sb/Pb or Si/Al). The eutectic diagram is characterized by the eutectic mixture (the lowest melting temperature composition) and by the melting temperatures of the pure compounds. In the temperature composition diagram we find a horizontal line (solidus line) below which only solid is present (pure A + pure B). The liquidus lines running from the eutectic point to the melting points of the pure compounds represent the conditions at which solid first forms from the liquid. Between one of the liquidus lines and the solidus line we have a two-phase region (solid A or B and liquid). If both compounds have the same enantiotropic mesophase, a further phase line mesomorphic/isotropic lies above the liquidus lines. In the two-phase region we have solid A or B and the mesophase, above the liquidus lines the mesophase, and above the clearing line the isotropic liquid. In binary mixed systems in which an enantiotropic transition changes into a monotropic one, the simple eutectic phase diagram gets

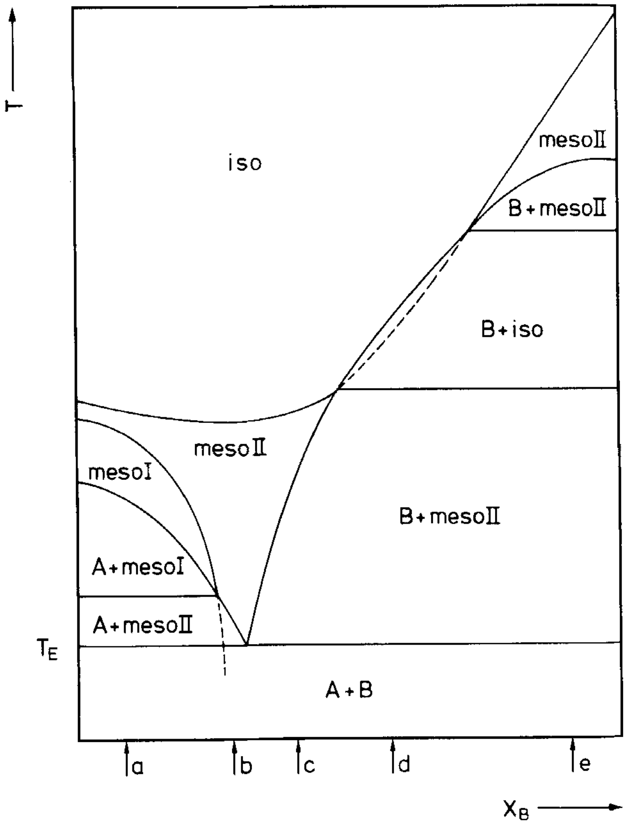

FIGURE 1 Eutectic phase diagram with different intersections between a phase equilibrium line and a liquidus line. Two-phase regions (meso I/meso II and meso II/iso) are omitted (also in Figs. 2, 3 and 5).

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. 1 shows a simple eutectic phase diagram with the liquidus lines intersected by different phase equilibrium lines. Below the solidus line there are two solid phases: pure A + pure B. At T_E the eutectic composition melts into mesophase II. Above the solidus line, system a splits up into the two phases solid A + meso II. Heating up, more A melts and the composition of the mesophase becomes more rich in A. At the temperature where the liquidus line crosses the phase equilibrium meso I/meso II, we get a *new phase equilibrium line:* the part of the mixture already melted into mesophase II now changes into mesophase I. Now we enter the two-phase region A + meso I. Heating up, more and more A melts, until at the liquidus line all A is melted. Only mesophase I remains. Further temperature elevation brings the sample into the region of mesophase II and finally into the isotropic liquid. The temperature where the two-phase region A + meso II changes into the two-phase region A + meso I is only determined by the temperature where the phase equilibrium line meso I/meso II intersects the liquidus line. Consequently, we get a *horizontal* phase equilibrium line which separates two two-phase regions. To the left of this intersection point, all mixtures have an enantiotropic mesophase I between the liquidus line and mesophase II. However, since at the eutectic temperature T_E the eutectic composition of all possible mixtures melts into mesophase II, there must be for all of these mixtures a phase equilibrium line where the melted mesophase II becomes mesophase I. Heating up system b, we enter the two-phase region A + meso II at T_E. Because system b lies to the right of the intersection point, we have only one enantiotropic mesophase (meso II). Heating up, more and more A melts until at the liquidus line all A is melted into mesophase II. Further temperature elevation finally brings the sample into the isotropic liquid.

System c lies to the right of the eutectic composition. At T_E we now come into the two-phase region solid B + meso II. Temperature increase brings the sample first into the region of the mesophase II and then into the isotropic liquid.

The behaviour of system d is a bit more complex because it has only a monotropic mesophase II. Heating up such a sample above T_E we enter the two-phase region B + meso II. Further temperature elevation causes more and more B to melt. At the temperature where the clearing line intersects the liquidus line, the mesophase transforms into the isotropic liquid. Now we have a two-phase region B + iso. Above the liquidus line, we finally are in the region of the isotropic liquid. For all mixtures to the right of this intersection point, we get a further horizontal phase equilibrium line, which separates the two two-phase regions B + meso II and B/iso. System e shows a still more complex behaviour. Because compound B has an enantiotropic mesophase II, the phase equilibrium line must intersect the liquidus line twice. Heating up such a mixture we run across three two-phase regions above T_E: B + meso II, B + iso, B + meso II (all separated by horizontal equilibrium lines).

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[2 - 5], they are missing in many published phase diagrams of binary eutectic mixed systems with such an intersection point[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.

3. 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-pentylbenzoyloxy)-benzoate (PCPB), Eastman, were purified by recrystallizing the samples several times in an appropiate solvent.

The measurements of the phase transition temperatures were made by DSC investigations (DSC-2, Perkin-Elmer) as well as by polarization microscopy (Leitz Ortholux II - POL BK with Mettler heating stage FP 5/52).

4. RESULTS

Three 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 (like example d), 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

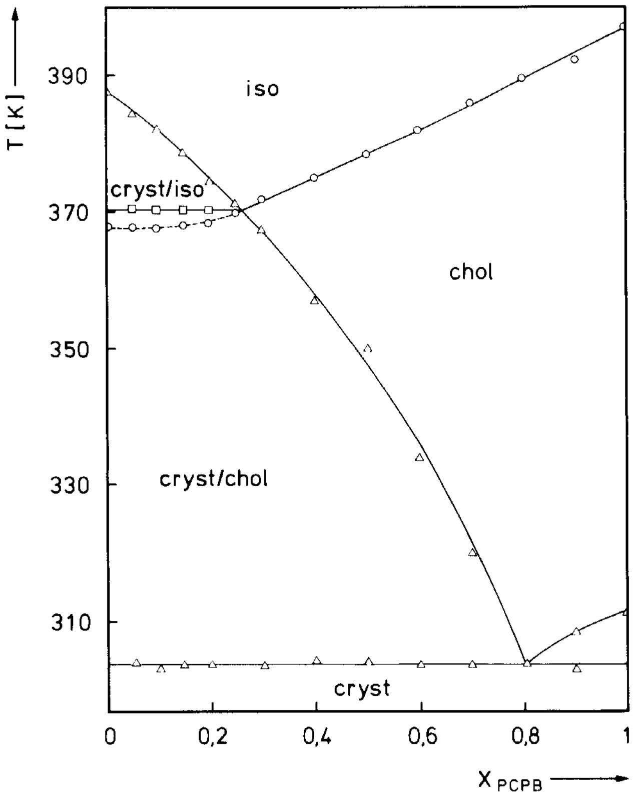

FIGURE 2 Phase diagram of the mixed system Ch-2/PCPB.

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. Figs. 2 + 3 show two different mixed systems 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[17]. In sample A the cholesteric mesophase is enantiotropic. The thermogram shows the eutectic peak,

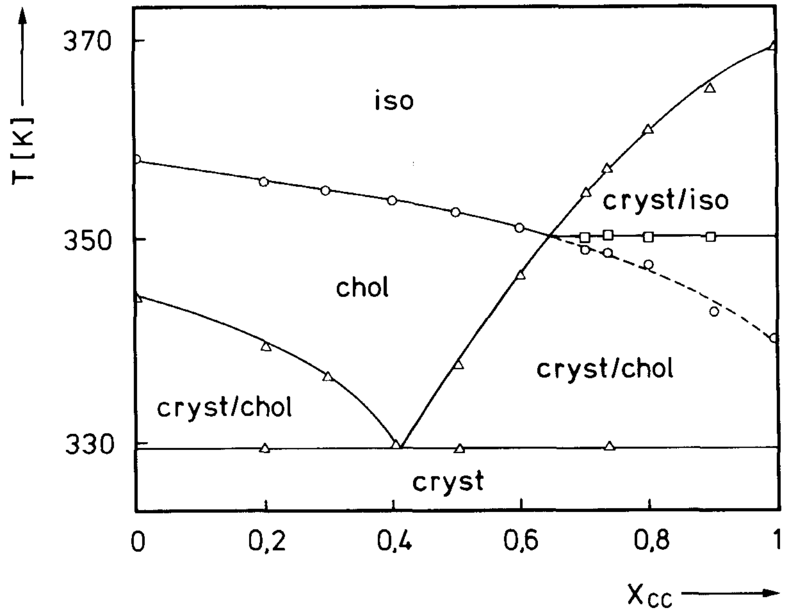

FIGURE 3 Phase diagram of the mixed system CCH 7/CC.

the melting peak, and the isotropic 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 is very difficult by means of polarization microscopy. However, we can detect these transitions in the DSC traces. In Fig. 6 two DSC thermograms of different mixtures

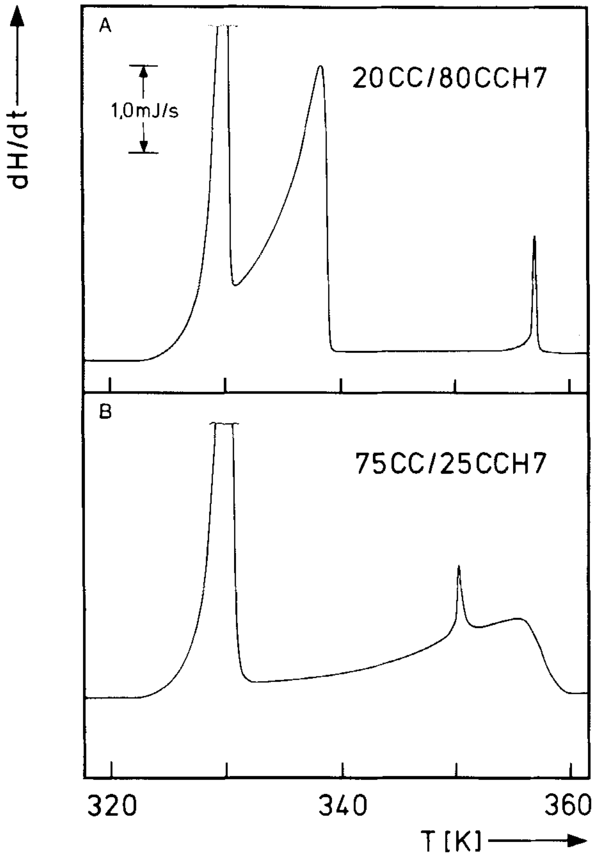

FIGURE 4 DSC-traces of two different compositions of the system CCH 7/CC. Sample mass ca. 5.5 mg, heating rate 5 K/min.

of the system Ch-14/PCPB are given. Mixture A has an enantiotropic smectic A and an enantiotropic cholesteric phase (like example a in Fig. 1). 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 part of the sample transforms

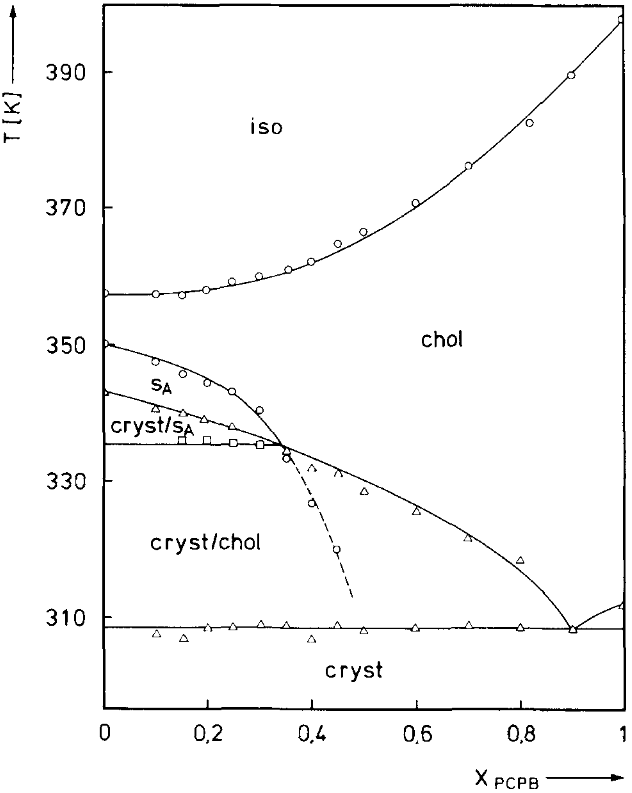

FIGURE 5 Phase diagram of the mixed system Ch-14/PCPB.

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 (like example b in Fig. 1). At 308 K the eutectic composition goes into the cholesteric state. Heating up, more and more Ch-14 becomes cholesteric. Above the liquidus line the whole sample is cholesteric. At 364 K the sample goes into the isotropic liquid. The small transition peaks close below the isotropic transition show

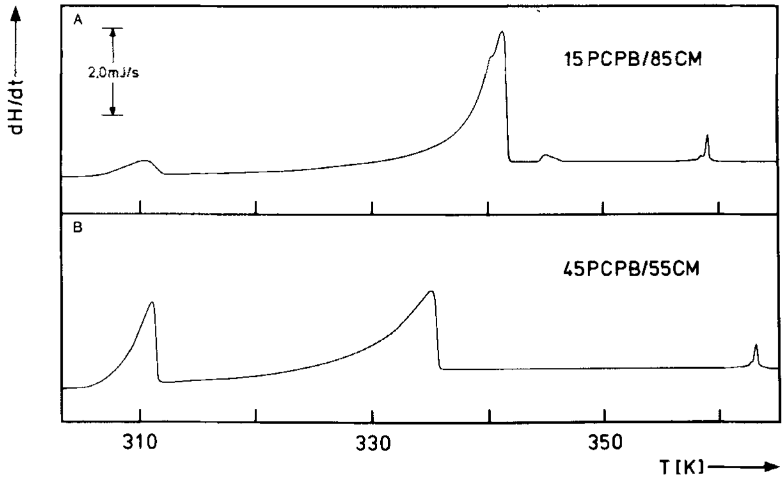

FIGURE 6 DSC-traces of two different compositions of the system Ch-14/PCPB. Sample mass ca. 10 mg, heating rate 1.25 K/min.

the transition cholesteric → Blue Phase[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.

5. 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[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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