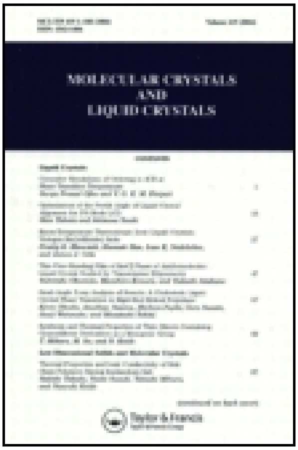

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Phase Diagrams of Mixtures Consisting of Polar Compounds S_E and $S_{A\ d}$

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PHASE DIAGRAMS OF MIXTURES CONSISTING OF POLAR COMPOUNDS S_E AND S_{A_d}

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Abstract Phase diagrams have been determined for binary mixtures of 4-dodecyloxy-4′-cyanobiphenyl (12OCB , smectic A_d) and 4-pentyl- or 4-heptyl-4′-isothiocyanatobiphenyl (5BT or 7BT, smectic A_E).The S→I, S→N and N→I phase transition enthalpies of these mixtures have been measured. It has been found that the smectic phases are separated by a nematic gap, and that the enthalpies ΔH_{S_E-I} and ΔH_{S_E-N} rapidly decrease with the increasing proportion of 12OCB.

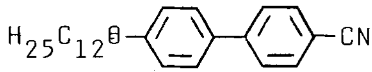
INTRODUCTION

Recently it has been observed that the nematic phase may be induced in binary mixtures of polar smectic compounds [1,2,3,5]. Such behaviour was observed for compounds with a smectic S_A or S_C phase and recently in mixtures of S_E and S_A smectics[4]. In order to aquire better knowledge of the properties of systems composed of smectics E and A we measured the variation of enthalpy of the phase transition points as a function of the mixture composition.

EXPERIMENTAL

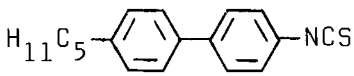
Materials

To obtain the binary mixtures the following compounds were used (see ref.4):



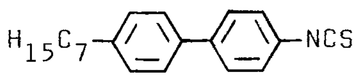
(12OCB)

C_1 57 C_2 69 S_{A_d} 89.9 I ; $\Delta H_{S\to I}$=4.6 kJmole^{-1} ;
l=2.87 nm; d=4.02 nm



(5BT)

C 53 S_E 74.5 I; $\Delta H_{S\to I}$=9.6 kJmole^{-1}; l=2.1 nm; d=2.0 nm



(7BT)

C 54 S_E 76 I; $\Delta H_{S\to I}$=8.8 kJmole^{-1}; l=2.35 nm; d=2.26 nm

Measurement

The phase diagrams were determined by the single concentration method. The phase transition points of the compounds and their mixtures were determined by the PZO "Biolar" polarization microscope with a THM-600 Linkam heated stage and a Unipan 600 microcalorimetr with a DSC device. The phase transition enthalpies were measured by the DSC method, and the smectic layer spacings by the X-ray method.

RESULTS

The phase diagrams of the 5BT-12OCB and 7BT-12OCB binary mixtures are shown in Figure 1a and 1b, respectively. The first of these diagrams (Figure 1a) shows a wide nematic gap separating the smectic E and A_d regions. The second diagram reveals induction of the nematic phase without separation of the smectic regions by nematic gap. The difference in the concentration range in which the

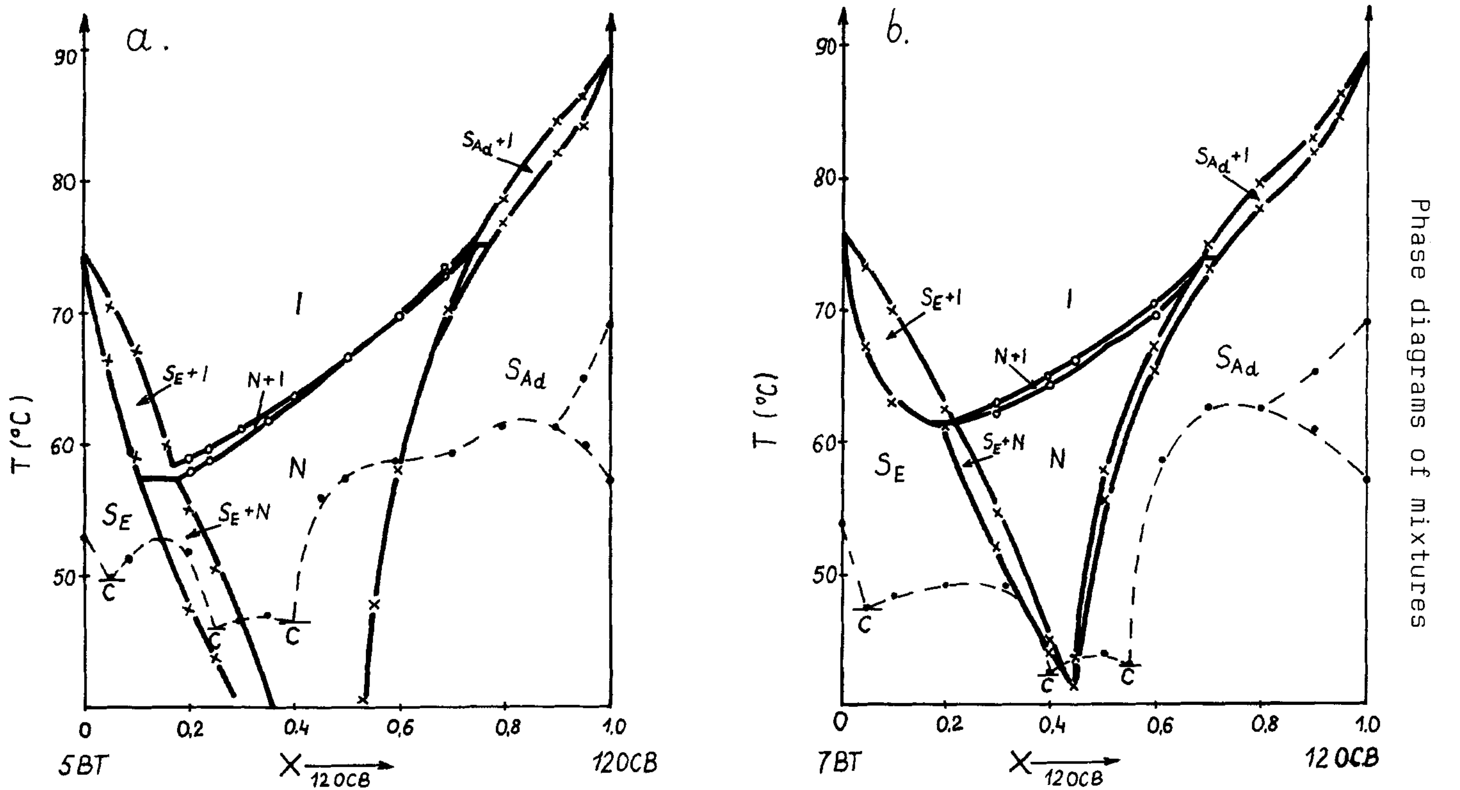


Figure 1 Phase diagrams for the binary systems: a)5BT-12OCB;b)7BT-12OCB.

nematic phase occurs in these two systems is related, as it was shown earlier[1,4], to the decrease of the smectic layer spacing ratio ($d_{S_{A_d}}/d_{S_E}$) of the mixture components which amounts to 2.01 and 1.78 for the 5BT-12OCB mixtures, respectively. The range of the induced nematic phase is affected in a lesser extent by the high, but comparable, S_{E-I} phase transition enthalpies (9.6 and 8.8 kJ $mole^{-1}$) of compounds 7BT and 5BT. The high energy with which the molecules are bonded in the smectic E phase is manifested by the wide temperature intervals in which the S_E and nematic or S_E and isotropic phases coexist in equilibrium.

The melting point curves of 7BT-12OCB and 5BT-12OCB mixtures are complicated since the mixtures do not form simple eutectics. The DSC curves of the 7BT-12OCB and 5BT-12OCB mixtures show in the heating cycle the existence of an exothermal effect. This suggests the formation of intermolecular compounds whose creation enthalpy is greater than that of crystal melting.

In Figure 2 the variation of the S→I (Figure 2a) and N→I (Figure 2b) phase transition enthalpy with the concentration of the compounds for the 7BT-12OCB (solid line) and 5BT-12OCB (dashed line) mixtures is presented. The enthalpy of the smectic-isotropic liquid phase transition decreases rapidly with the increase of the concentration of the second component in the mixture. The lowering of the enthalpy of the S_{A_d-I} phase transition is comparable with that observed in mixtures of A_d and A_1 smectics[1], whereas the decrease of enthalpy of the $S_{E\to I}$ phase transition is very rapid (from 8.81 $kJmole^{-1}$ for pure 7BT to 0.55 $kJmole^{-1}$ for the mixture containing 90% mole 7BT). The lower content of the compound hawing the smectic A_d phase results in a much greater destabilization of the

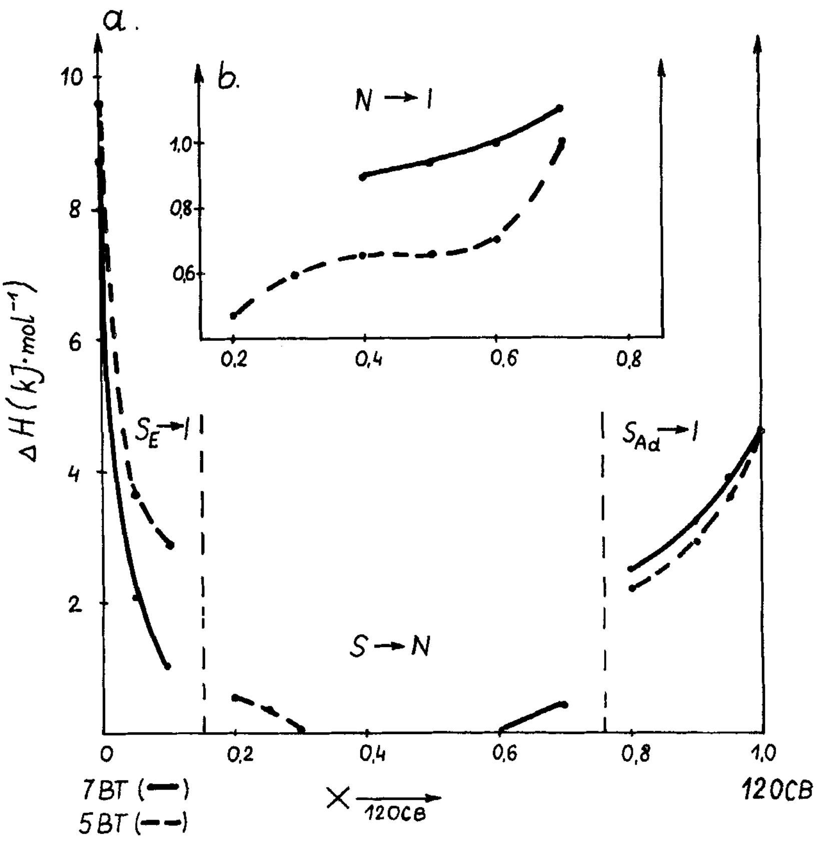


Figure 2 Enthalpies of S–I or S→N (a) and N→I (b) transitions of the systems 5BT–12OCB, 7BT–12OCB.

smectic E phase as compared with the smectic A one[1]. The enthalpy of the S_E→N phase transition also decreases rapidly for the 5BT–12OCB mixture; this transition passes from the transition of the first kind to, nonmeasurable by the DSC technique, the second kind transition, whereas the S_{A_d}→N phase transition is in the whole range of exis-

tence of the nematic phase a transition of second kind. In the case of the 7BT-12OCB mixture the S_E→N phase transition is in the whole range a transition of the second kind, and the enthalpy of the S_{A_d}→N phase transition assumes small values.
The N→I transition enthalpies vary for both mixtures with the change of composition analogously as it was described in ref. (1).

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