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A nematic phase created in mixtures of polar smectics The effect of smectic layer properties

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Phase diagrams of binary mixtures composed of compounds with the NCS terminal group (*n*-DBT, *n*-PBT, *n*-TPB (smectic A_1) or *n*-BT (smectic E_1)) and *n*-OCB, *n*-CB (smectics A_d) are presented. It is shown that the width of the nematic gap that separates the A_1 or E_1 phase region from the smectic A_d phase is related to the interaction energy of the molecules in the smectic layers and to the difference in the smectic layer spacings.

1. Introduction

In our earlier work we have shown that the A_1 and A_d smectic phases may be strongly destabilized in mixtures of polar compounds if the senses of the dipole moments of the polar groups of the molecules coincide [1] and the smectic layer spacings differ [2-4]. Continuing our research into the effect of different factors on the destabilization of smectic layers, we show, in the present work, that the nematic phase is created also in mixtures composed of smectics E_1 and A_d and that the nematic gap observed between the regions of the smectic A_1 or E_1 phase and the smectic A_d phase is determined both by the smectic layer spacing ratio of both components of the mixture and by the interaction energy of the molecules in the smectic layers.

2. Experimental

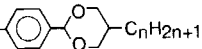
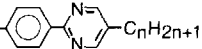
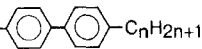
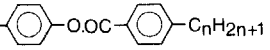
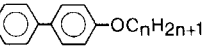
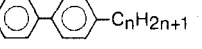
The compounds studied and their major properties are summarized in the table. These compounds were synthesized and carefully purified in our laboratory, except for *n*-PBT, which was supplied by Dr Schadt of Hoffman La Roche.

The phase diagrams of the binary mixtures were determined by the single-concentration method. The transition temperatures of all the compounds and their binary mixtures were determined by means of a VEB Analytik (Dresden) polarization microscope with a hot stage and a Unipan 600 microcalorimeter with a D.S.C. attachment.

3. Results

Fragments of the phase diagrams of the binary mixtures relating to the SI, NI and NS phase boundaries are shown in figures 1-3. In the figures the experimental $S_A \rightarrow I$ and $S_A \rightarrow N$ transition temperatures are marked by crosses, and the $N \rightarrow I$ by full circles. Figure 1 relates to the 4PBT-8OCB, 4PBT-12OCB and 4PBT-12CB binary mixtures. Compounds 8OCB, 12OCB and 12CB form smectic A_d phases, and the d/l ratios are 1.37, 1.40 and 1.44 respectively. The molecular binding energy in the smectic A_d layer of 12OCB and 12CB are similar ($\Delta H_{S_A N} \approx 3.0 \text{ kJ mol}^{-1}$). These values were obtained by deducting the estimated values of virtual $N \rightarrow I$ phase

Investigated smectic compounds and their properties

Formula	<i>n</i>	Transition temperature/°C	ΔH_{SN} or $\Delta H_{SI}/\text{kJ mol}^{-1}$	<i>l</i> /nm	<i>d</i> /nm
SCN-  -C _n H _{2n+1} <i>n</i> -DBT	4	C 61 S _{A1} 76.5 I	4.0	1.98	1.82
SCN-  -C _n H _{2n+1} <i>n</i> -PBT	4	C 61 S _{A1} 77 I	3.8	1.95	1.83
SCN-  -C _n H _{2n+1} <i>n</i> -BT	4 5 6 7	C 67 S _E 82 I C 53 S _E 74.5 I C 34 S _E 75 I C 54 S _E 76 I		1.95 2.10 2.22 2.35	1.86 2.00 2.14 2.26
SCN-  -C _n H _{2n+1} <i>n</i> -TPB	4 6 7	C 60 (37.5 S _{A1}) I C 52 (49.5 S _{A1}) I C 62.5 (57 S _{A1} , 57.5 N) I		2.14 2.38 2.50	
NC-  -OC _n H _{2n+1} <i>n</i> -OCB	8 12	C 54.5 S _{A_d} 67.5 N 81 I C 57 K ₂ 69 S _{A_d} 89.8 I	0.022 4.6	2.34 2.87	3.20 4.02
NC-  -C _n H _{2n+1} <i>n</i> -CB	12	C 45 S _{A_d} 58.5 I	4.0	2.76	3.98

transition enthalpy of 12OCB or 12CB from the experimental values for the S_A → I transitions. $H_{(N \rightarrow I)_{vir}}$ of 12OCB or 12CB are equal 0.6–1 kJ mol⁻¹ [5] and they are the same as N → I enthalpies of ordinary nematics). The corresponding energy in a layer of 8OCB is very small ($\Delta H_{S_A N} = 22 \text{ J mol}^{-1}$). For all three pairs of binary mixture a nematic gap is observed separating the smectic A₁ and A_d regions. The width of this gap is similar for the 4PBT–12OCB and 4PBT–12CB mixtures but smaller than for 4PBT–8OCB pair. The smectic A_d phase is destabilized the most in 8OCB. The smectic A₁ phase in 4DBT is less destabilized in the mixture with 8OCB than in the mixtures with 12OCB or 12CB. The ratio, *r*, of the smectic A_d layer spacing to that of S_A, for the pairs of compounds 4PBT–8OCB, 4PBT–12CB, and 4PBT–12OCB increases in the order 1.74, 2.17 and 2.19. Hence we see that for the mixtures given in figure 1 the smectic A_d phase is not destabilized with increasing ratio *r*, but with decreasing interaction energy of the molecules in the smectic layer when this energy is equated with the S_{A_d} → N transition enthalpy. In contrast, the smectic A₁ phase in 4PBT is destabilized with increasing ratio *r*.

The behaviour of the pairs of compounds 7DBT–8OCB and 7DBT–12OCB described in [5] is analogous.

In figure 2(a) fragments of the phase diagrams for mixtures 8OCB–4TPB, 8OCB–6TPB and 8OCB–7TPB are compared, while in figure 2(b) those of analogous mixtures are shown in which 12OCB is the constant component. The mixtures of the first series have a very wide nematic gap which increases with the growing smectic layer spacing ratio (for the pairs of compounds: 8OCB–4TPB, 8OCB–6TPB and 8OCB–7TPB the ratio *r* is 1.56, 1.40 and 1.34, respectively). A similar relationship between the nematic gap width and *r* is observed for mixtures with 12OCB (see figure 2(b)). In the latter case the width of the nematic gap is smaller despite the

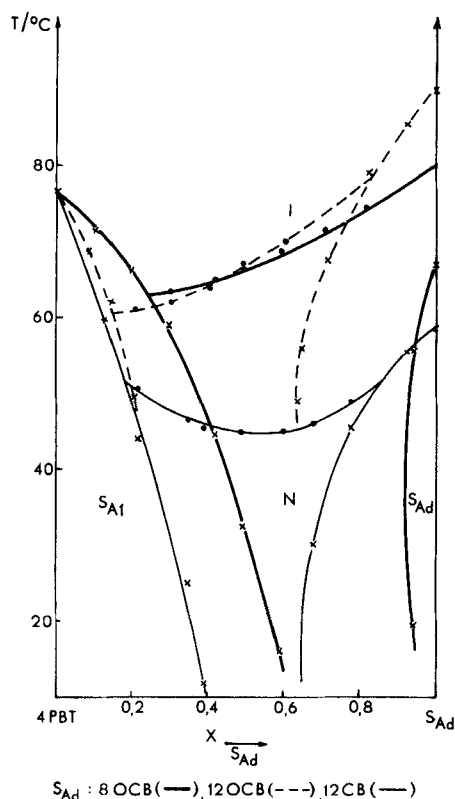


Figure 1. Comparison of nematic phase creation in binary systems of smectics A_1 and A_d .

increase of r to 1.96, 1.76 and 1.68, respectively. This is due to the greater enthalpy of the $(S_A \rightarrow I)_{vir}$ phase transition in 12OCB as compared with that of the $S_A \rightarrow N$ phase transition in 8OCB.

The diagrams shown in figure 2 for n -TPB differ from those shown in figure 1 for 4-PBT in that the smectic phase is much more destabilized for n -TPB as compared with 4-PBT, and the nematic gap widens at the cost of the smectic A_1 phase region. This occurs because the interaction energy of the molecules in a smectic layer of n -TPB is smaller than for 4PBT. For the series of esters n -TPB an accurate value of the transition enthalpy is known only for the compounds 6TPB and 8TPB [6] and amounts to about 2 kJ mol^{-1} . We did not succeed in accurately determining these enthalpies for the esters 4TPB and 7TPB, in the first case because of its strongly monotropic character, and in the second because of the close proximity of the $S_A \rightarrow N$ and $N \rightarrow I$ transitions. The values determined approximately show that the interaction energy of the molecules in the smectic layer is also similar in these compounds to that found for 6TPB. It seems therefore reasonable that this energy does not depend to a large degree on n , as observed for the compound from the homologous series, n -DBT [7].

In figures 3(a) and (b) fragments of phase diagrams are compared for mixtures in which one component is 8OCB or 12OCB and the other is one of the n -BT compounds with n varying from 5 to 7. The compounds n -BT are smectics E and have a large molecular interaction energy in the crystal lattice ($\Delta H_{S_E \rightarrow I} \approx 10\text{ kJ mol}^{-1}$). This

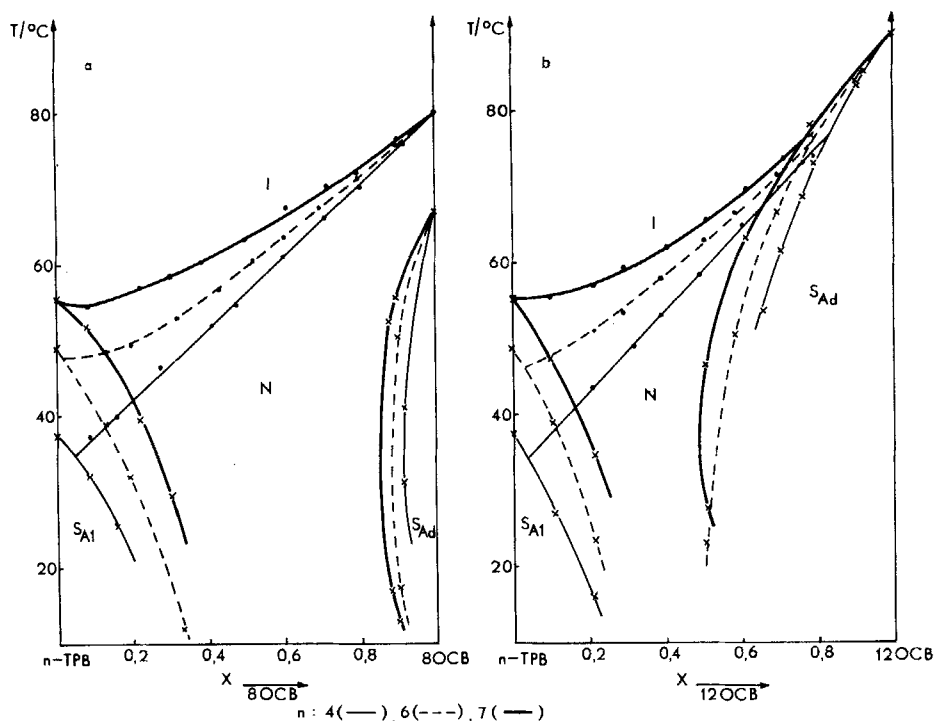


Figure 2. Effect of smectic layer spacing ratio and smectic phase transition enthalpy on creation of nematic phase in the n -TPB-8OCB and n -TPB-12OCB systems.

manifests itself in a wide temperature interval of coexistence of smectic E and isotropic phases. In figure 3 the two-phase region is not shown, but only the upper temperature at which the smectic phase appears. For all the mixtures containing compounds from the series n -BT, where n varies from 5 to 7, a narrow nematic gap is observed whose width decreases systematically with decreasing smectic layer spacing ratio. For the binary mixtures 7BT-8OCB, 6BT-8OCB and 5BT-8OCB the values of r are 1.36, 1.50 and 1.60 respectively. A similar dependence on r is observed for the mixtures n -BT-12OCB (see figure 3b). The observed nematic gap between the regions of phases S_E and S_{A_d} is smaller for the mixtures n -BT-12OCB than for those with 8OCB, and for the pair 7BT-12OCB it is no longer observed; in this series r has the values 1.78, 1.87 and 2.01 for the successive pairs arranged according to increasing n . There are also other differences between the phase diagrams of the series n -BT-8OCB and n -BT-12OCB:

- (i) The smectic E phase is destabilized less in the first series of mixtures than in the second; this is due primarily to the different values of the r ratio in both series.
- (ii) The nematic gap lies in the first series in the concentration range of 0.6–0.9 mole fraction of 8OCB, and in the second series in the concentration range of 0.4–0.6 mole fraction 12OCB.

The different positions of the nematic gap in both series of mixtures result because the stabilities of the S_{A_d} phases in 8OCB and 12OCB are different and because the

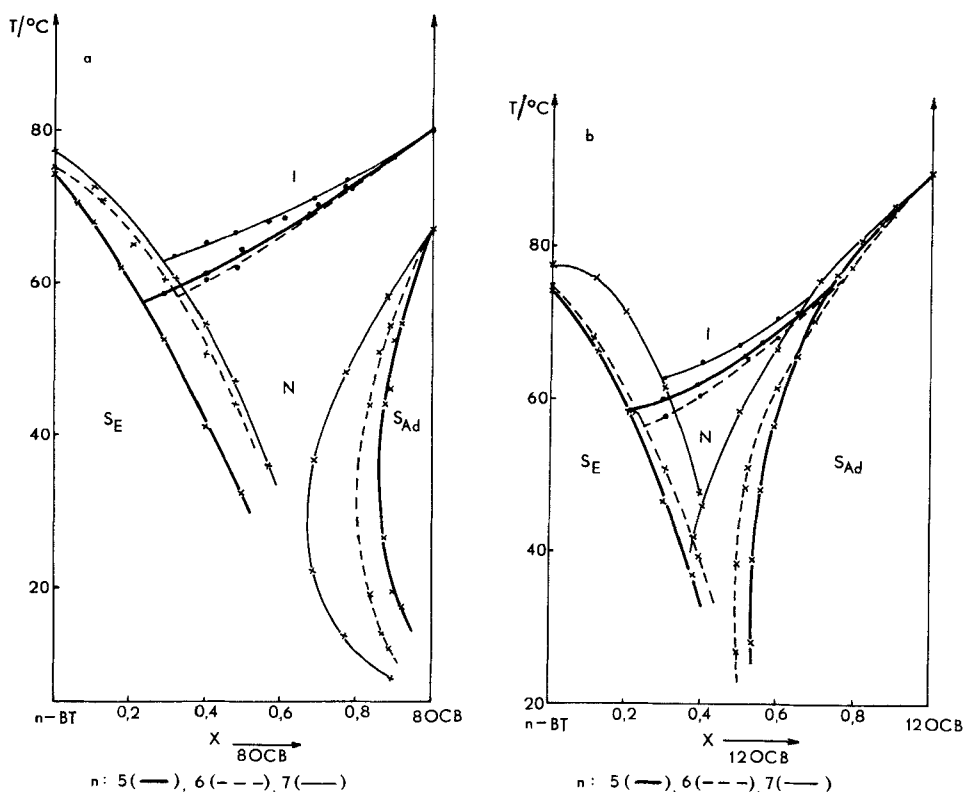


Figure 3. Creation of nematic phase in binary systems of smectics A_1 and E.

destabilizing capacities of these two compounds with respect to the S_E phase in the n -BT series vary.

4. Conclusions

The results presented in figures 1–3 show that the observed strong destabilization of the smectic phases in mixtures of polar compounds, manifesting itself under definite conditions by the creation of the nematic gap that completely separates the smectic regions, depends on two major factors: the ratio of the layer spacing of the smectic A_d to that of smectic A_1 or E; and the molecular interaction energy in the smectic A_1 , E and A_d layers. These two factors determine the width of the nematic gap and its position in the concentration range.

The destabilization is greater the larger the smectic layer spacing ratio of the components of the mixture. This relationship is best seen in binary systems in which one of the components is a compound from the homologous series in which the enthalpy $\Delta H_{S_{A-1}}$ depends weakly on the length n of the alkyl chain.

Enhancement or induction of the nematic phase is more difficult the greater the molecular interaction energy in the smectic layer. This relationship is illustrated by the mixtures shown in figures 1 and 4. In figure 1 systems are compared in which the compounds with the smectic A_d phase differ as regards the enthalpy of the $S_{A_d} \rightarrow I$ or $S_{A_d} \rightarrow N$ phase transition, and in figure 4 those in which the compounds with the S_{A_1} and S_E phase differ as regards the enthalpy of the transition from the smectic to the isotropic phase.

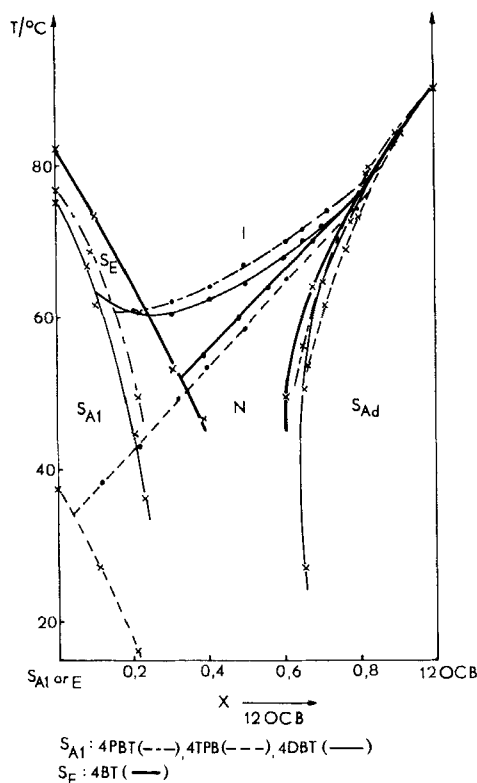


Figure 4. Effect of smectic phase transition enthalpy on creation of nematic phase.

The results obtained suggest, in addition, that from binuclear smectic compounds we can easily obtain a nematic mixture whose clearing point lies in the range 60–70°C. The multicomponent mixture may reveal an arbitrarily low temperature of melting directly to the nematic phase. An example of such a mixture is the following:

(1) composition	mole ratio
4DBT	0.212
6DBT	0.399
8OCB	0.176
12OCB	0.006
12CB	0.215
10CPH	0.092
(2) clearing point	57°C
(3) melting point	–5°C
(4) viscosity at 20°C	48 mPa s
(5) dielectric anisotropy	+8.6

In addition on the basis of results obtained so far, we can believe that the geometric and energetic factors are decisive for the destabilization of the smectic phases. The chemical structure of the compound has only an indirect effect in that it determines the character of the smectic phase and the molecular interaction energy in the smectic layer.

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