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Effect of properties of the smectic A_d phase on the induction of a nematic phase in binary mixtures of smectics A_1 and A_d

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The phase diagrams of two series of binary mixtures composed of 5-trans-*n*-butyl-2-(4-isothiocyanatophenyl)-1,3-dioxane (smectic A_1) and 4-(trans-4′-*n*-alkylcyclohexyl)-1-(2-cyano-ethenyl)benzene or 4-cyanophenyl-4′-*n*-alkoxybenzoates (both smectic A_d) are determined. It is shown that the smectic layer spacing ratio and smectic phase transition enthalpy are the factors influencing the width and the position of the nematic gap created between the two smectic regions. It is found that their influence on this ability is in the opposite direction.

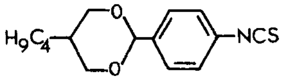
1. Introduction

In the binary systems composed of smectic compounds, in which the nematic phase was induced or enhanced at the cost of the smectic phase investigated so far, we always observed the enhancement of the nematic phase with the increase of the smectic layer spacing ratio of the components [1–3]. Recently Pelzl *et al.* [4] have obtained phase diagrams of binary mixtures in which the concentration interval, over which the induced nematic phase exists, decreases with increases in the length of the smectic A_d molecules, i.e. with increase of the smectic layer spacing ratio for the components. We undertook this work to find out why these results are incompatible with ours.

2. Experimental

2.1. *Materials*

In all the binary systems studied 5-trans-*n*-butyl-2-(4-isothiocyanatophenyl)-1,3-dioxane (4DBT), which has an enantiotropic smectic A_1 phase, was the constant component [1]



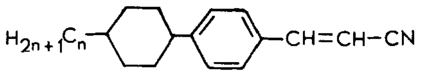
(4DBT)

$$\mathrm{C}\ 61^\circ\mathrm{C}\ \mathrm{S}_{\mathrm{A_1}}\ 76{\cdot}5^\circ\mathrm{C}\ \mathrm{I}\ \Delta H_{\mathrm{S}\to\mathrm{I}} = 4{\cdot}0\,\mathrm{kJ/mol};\ l = 1{\cdot}98\,\mathrm{nm};\ d = 1{\cdot}82\,\mathrm{nm}.$$

The second component has always one with a smectic A_d phase selected in such a way that either the change of the smectic A_d spacing ratio was accompanied by an increase of enthalpy of the $S_{A_d} \rightarrow N$ phase transition (series I), or the spacing of the smectic A_d was constant but the enthalpy of the $S_{A_d} \rightarrow N$ or $S_{A_d} \rightarrow I$ phase transition varied (series II).

In series I the second component was a compound from the homologous series 4-(trans-4′-*n*-alkylcyclohexyl)-1-(2-cyano-ethenyl)benzene (*n*EPCH) [5]. The transition temperatures, the enthalpy fo the S → N phase transition, the molecular length

Phase transition temperatures, enthalpies of the S_d–N transition, molecular lengths and smectic layer spacings for compounds of the 4-(trans-4′-*n*-alkylcyclohexyl)-1-(2-cyano-ethenyl)-benzene homologous series

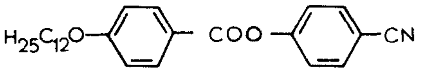


(nEPCH)

	Transition temperature/°C									
n	C		S_{A_d}		N		I	$\Delta H_{S\to N}$/J mole^{-1}	*l*/nm	*d*/nm
4	●	57	●	(32)	●	144	●	0	2·04	–
5	●	49	●	61	●	149·5	●	0	2·19	2·87
6	●	54	●	106	●	144	●	74	2·29	3·07
7	●	39	●	120	●	143·5	●	93	2·43	3·27
8	●	48	●	128	●	137·5	●	135	2·54	3·42

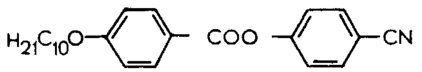
and the smectic layer spacing of the nEPCH compounds are summarized in the table. The compounds of the nEPCH homologous series have both nematic and smectic A_d phases; the enthalpy and the transition temperatures of the lattice increase with n. In compounds 4EPCH and 5EPCH the $S_{A_d} \to N$ phase transition is second order ($\Delta H \approx 0$). In compounds 6EPCH, 7EPCH and 8EPCH the enthalpy of the $S_{A_d} \to N$ phase transition takes the values 74, 93 and 135 J/mol, respectively.

In series II the second component of the mixture was one of the following p-cyanophenyl alkyl- or alkoxybenzoates:



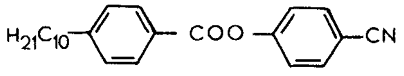
(12.0.CN)

C 73°C S_{A_d} 89°C I $\Delta H_{S\to I}$ = 3·8 kJ/mol; *l* = 3·1 nm; *d* = 3·63 nm;



(10.0.CN)

C 79°C S_{A_d} 79·5°C N 86°C I, $\Delta H_{S\to N}$ = 0 kJ/mol; *l* = 2·85; *d* = 3·63 nm;



(10.CN)

C 59·5°C (S_{A_d} 55·3°C) N 60°C I, $\Delta H_{S\to N}$ = 0 kJ/mol; *l* = 2·72 nm; *d* = 3·68 nm.

These esters differ only slightly as regards their smectic layer spacings, but the molecular interaction energies in the smectic layers vary significantly.

2.2. *Measurement*

The transition temperature of all the compounds and their mixtures were determined with a VEB Analityk Dresden polarization microscope and a Unipan 600 microcalorimeter with D.S.C. equipment. The enthalpies of the phase transitions were measured by the D.S.C. method, and the smectic layer spacings by the X-ray method. All the phase diagrams were obtained by the single concentration method.

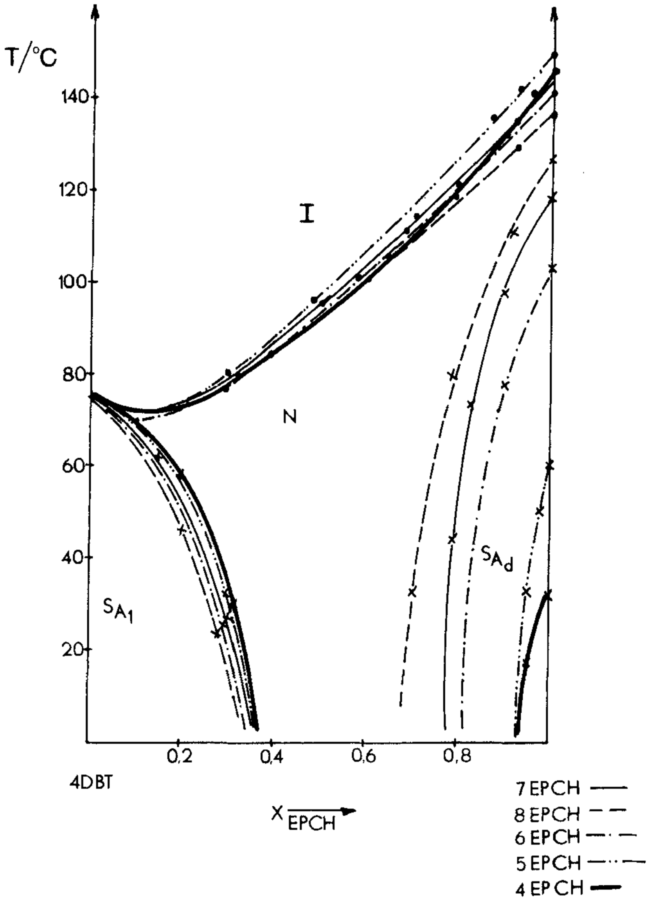


Figure 1. Fragments of the phase diagrams for the binary systems 4DBT *n*EPCH.

3. Results

In figure 1 we show fragments of phase diagrams for the series *n*EPCH –4DBT. In this series we observe, as in [4] that the range of the nematic gap decreases with the growing length of the A_d smectic molecule, i.e. with increasing smectic layer spacing ratio $(d_{S_{A_d}}/d_{S_{A_1}})$. This is due to the increase of the smectic A_d-nematic transition enthalpies and temperatures in compounds that are successive members of the nEPCH homologous series, and hence to its greater resistance to destabilization in mixtures with a smectic A_1 phase.

The influence the these parameters for the smectic A_d phase on the width of the nematic gap is even stronger in series II. In figure 2 we show fragments of the phase diagrams of binary mixtures composed of 4DBT and of 12.O.CN, 10.O.CN or 10.CN. Despite the almost identical smectic layer spacing ratios in all the mixtures studied, we observe the widest nematic gap for the 10.CN –4DBT system in which the molecular interaction energy in the smectic A_d lattice is the lowest (i.e. the lowest values of $\Delta H_{S_{A_d}\rightarrow N}$ and $T_{S_{A_d}\rightarrow N}$). As the interaction energy in the smectic A_d phase increases, we observe a narrowing of the nematic gap at the side of smectic A_d. It follows that the destabilization of the smectic A_d phase caused by 4DBT is much stronger in 10.CN than in 10.O.CN or 12.O.CN.

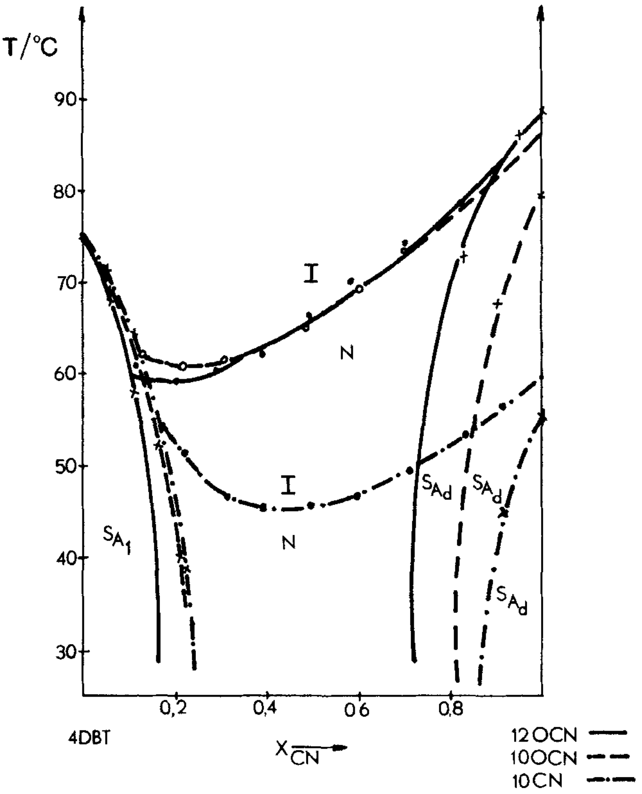


Figure 2. Fragments of the phase diagrams for the binary mixtures of 4DBT with 12.O.CN, 10.O.CN, 10.CN.

On the other hand, the smectic A_1 phase in 4DBT is stronger destabilized (i.e. lower S_A phase transition temperatures) by 12.O.CN than by 10.O.CN or 10.CN; this is in agreement with the expected sequence of stability of dimers in these compounds.

4. Discussion

The width of the nematic gap created between two smectic regions depends on the difference in the smectic layer spacings of the components, on the molecular interaction strength in the smectic layer, and on the difference in polarity of the components. If mixtures are made up from components selected in such a way that the smectic layer spacing ratio changes, but this change is not accompanied by a change of the molecular interaction energy in the smectic layer, then the smectic layer spacing ratio is decisive for the width of the nematic gap. Such systems were studied in [1, 2], where in the binary mixtures the component varied was the smectic A_1, which was always a compound from the nDBT series, while the smectic A_d was in all cases the same compound. It is characteristic of the compounds from the *n*DBT series that the enthalpy of the $S_{A_d} \rightarrow N$ phase transition is almost constant [1].

If the mixture is prepared from components selected so that their smectic layer spacing ratio is constant while the molecular interaction energy in the smectic layer varies, then the width of the nematic gap is greater the smaller is that interaction energy. Such a situation is observed in series II studied here. If the interaction energy in the smectic lattice and the smectic layer spacing ratio very simultaneously (e.g. the smectic lattice energy increases as does the smectic layer spacing ratio of the mixture components), then the effects of these factors on the destabilization of the smectic phase is opposite, and the resulting effect may vary depending which factor prevails. For instance, the width of the nematic gap may decrease though the smectic layer spacing ratio increases. Such behaviour is observed in series I of the mixtures studied here, and probably also for the compounds studied by Pelzl [4], though the latter conclusion is not certain since variations of the enthalpy for the S_{A_d} → N and S_{A_d} → I phase transitions of these compounds have not been measured.

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