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Intermediate nematic phases in binary systems with complex formation

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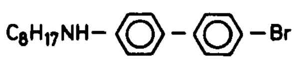
The phase diagrams of some binary systems of smectogenic compounds are presented in which intermediate nematic phases occur over a large concentration range. An attempt has been made to interpret this behaviour in terms of structural differences between the smectic A phases of the components.

1. Introduction

Intermediate liquid-crystalline phases are mixed phases which occur in a closed region of the temperature–concentration field [1, 2]. As shown in [2] it is expedient to distinguish *stabilized* and *induced* intermediate phases. Stabilized phases start from hypothetic (unstable) phases of one or both components. The term induced should be used if the phase boundaries exhibit pronounced maxima. Many examples of intermediate nematic phases are described in the literature [3–22]. It is interesting that the first intermediate nematic phase had already observed in 1907 by Vorländer and Gahren [3]. In this work we have studied binary mixtures with intermediate nematic phases where one component is always the same whereas the other is a member of a homologous series.

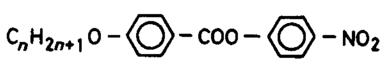
2. Materials

The compound which was used in all the binary systems was 4-*n*-octylamino-4′-bromo-biphenyl



C 52·5° C S_B 53·5° C S_A 55·8° C I

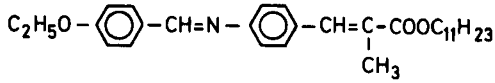
The transition temperatures in ° C of the homologous 4-nitrophenyl 4-*n*-alkyloxy-benzoates [23] are



n	C		S_A		N		I
8	·	50·2	·	61·6	·	68	·
9	·	63	·	71·3	—		·
11	·	66	·	81	—		·
14	·	72	·	86·5	—		·

See [24].

It can be seen from the table that for members with $n > 8$ the nematic phase disappears and only smectic A phases occur. For comparison, a smectogenic terminal non-polar compound was also combined with 4-*n*-octylamino-4′-bromobiphenyl: *n*-undecyl 4-(ethoxybenzylidene amino)-α-methylcinnamate [25].



C 63 S_A 82 I

This compound is the lowest member of this homologous series which does not exhibit a nematic phase.

3. Experimental

The phase diagrams were studied with a polarizing microscope (Ergaval, VEB Carl Zeiss Jena) by using the contact method [26] and by determination of the transition temperatures in mixtures of particular concentrations. The layer spacings of the smectic A phase were measured by X-ray investigations using small-angle equipment.

4. The phase diagrams

The phase diagrams studied are presented in figures 1 to 5. It is seen from the diagram in figure 1 that the binary system of 4-*n*-octylamino-4′-bromobiphenyl (*B*) with the octyloxy homologue of the series (*A*) the nematic phase of component A exists over a wide concentration range whereas the transition curve S_A–N exhibits a distinct minimum. The S_B phase of component *B* is restricted to mixtures with a high concentration of *B*. Although the higher homologues of component *A* (C_9, C_{11}, C_{14}) possess only smectic A phases the same type of phase diagram is obtained for the corresponding binary systems (cf. figures 2, 3 and 4). The only difference to figure 1 is that the nematic phase now is an intermediate phase. With increase in the

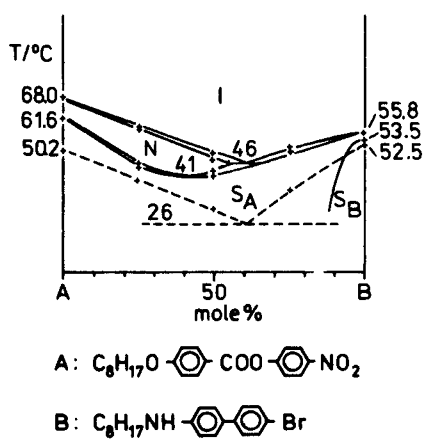


Figure 1. The composition–temperature phase diagram for the binary mixture with the components shown.

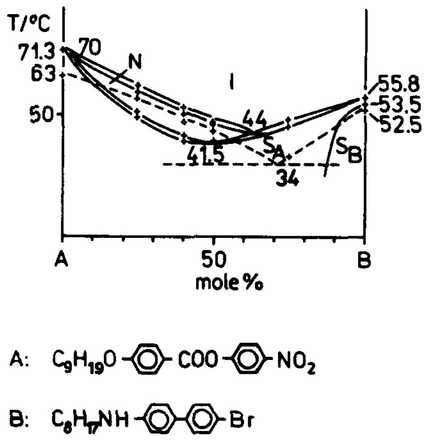


Figure 2. The composition–temperature phase diagram for the binary mixture with the components shown.

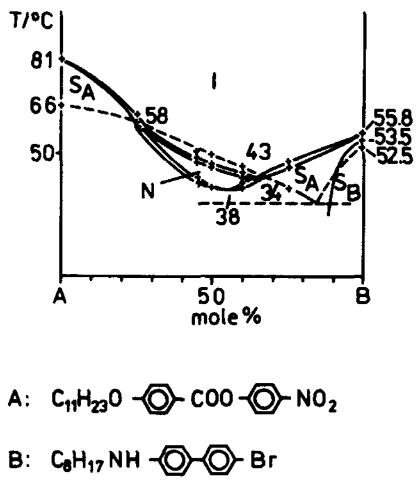


Figure 3. The composition–temperature phase diagram for the binary mixture with the components shown.

alkyl chain length of component *A* the concentration range of the nematic region decreases and is shifted to lower temperatures. Only for the nonyloxy homologue (cf. figure 2) is the intermediate nematic phase partially in the stable region. In the binary systems of the higher homologues (C_{11}, C_{14}) the intermediate nematic phase can be observed only by supercooling the isotropic liquid (cf. figures 3 and 4).

For comparison, we have studied the binary system of 4-*n*-octylamino 4′-bromobiphenyl with the terminal non-polar *n*-undecyl 4-(4-ethoxybenzylidene-amino)-α-methylcinnamate. This compound is the lowest member of the homologous series which does not possess a nematic phase. The phase diagram is shown in figure 5 and for the sake of clarity the melting curve is not drawn in the diagram. It is seen from figure 5 that the type of diagram is quite similar to those presented in figures 2 to 4. The only difference is that the smectic A phase of both components is not completely miscible, as in the binary systems of figures 1 to 4.

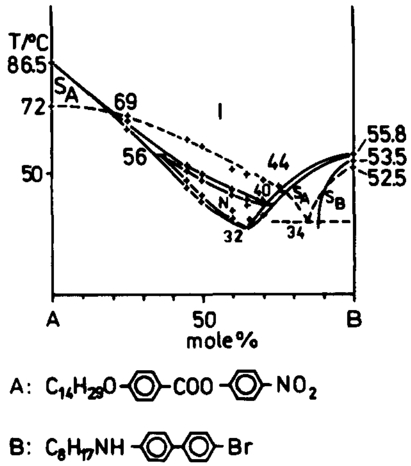


Figure 4. The composition–temperature phase diagram for the binary mixture with the components shown.

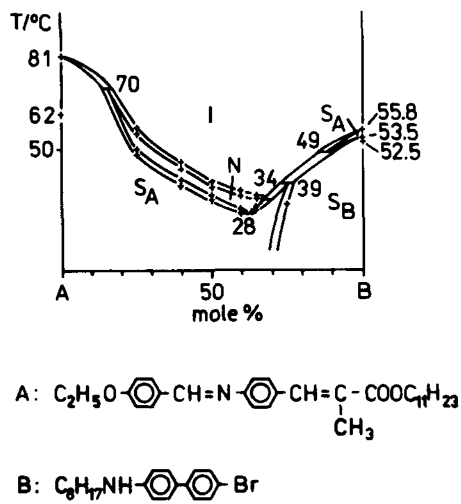


Figure 5. The composition–temperature phase diagram for the binary mixture with the components shown.

5. Discussion

There are some binary systems with intermediate nematic phases where both components exhibit no liquid-crystalline phases [3–5, 7, 9, 14, 16, 17]. In these cases the intermediate nematic phase is obviously starting from the virtual nematic phase of one or both components which is not detectable because of insufficient supercooling of the isotropic liquid. According to the definition given in [2] this intermediate nematic phase is a stabilized intermediate phase. In the binary systems reported in [14, 16, 17] the nematic–isotropic transition curve exhibits a maximum, obviously due to electron donor–acceptor interaction. In this case we can speak about stabilized *and* induced intermediate nematic phases. This first type of binary system where both components do not exhibit a liquid-crystalline phase, in our opinion is not really different from such cases where one or both components have monotropic nematic phases, as first described by Bogojawlenski and Winogradow in 1907 [27].

In most binary systems with intermediate nematic phases (also in the systems presented here) the mixing components form only smectic phases [6, 8, 10–13, 15, 18–22]. In such systems the nematic phase originates formally from *hypothetic* nematic phases of one or both components. The term hypothetic means that the nematic phase of the pure compound is thermodynamically unstable with respect to any smectic phase. In some cases this is indicated by the fact that the lower homologues of the smectogenic components (also in our binary system shown in figure 1) exhibit nematic phases (see [6, 10, 12, 15, 18–20]. In the binary systems presented here the nematic–isotropic transition curve is nearly linear and the smectic A–nematic curve shows a minimum similar to the binary systems described in [19, 20, 22]. Furthermore, the concentration range of the nematic phase decreases and is shifted to lower temperatures if the ratio of the molecular lengths of the components increases.

In the binary systems of the homologous 4-nitrophenyl 4-*n*-alkyloxybenzoates the isotropic and liquid crystalline phases exhibit electron donor–acceptor interactions, indicated by a yellow colour of the mixtures whereas the pure components are colourless. In this connection at first sight the occurrence of intermediate nematic phases is surprising because the electron donor–acceptor interaction generally favours the stabilization of the smectic state [28–30]. For example, in binary systems of 4-nitrophenyl 4-*n*-alkyloxybenzoates with 4,4′-bis-[pentylamino]-biphenyl induced smectic A phases were observed (see figures 2 and 3 in [28]). Only if the molecules have a special shape, and especially lateral branches, the induction of smectic phases can be suppressed [31].

The question arises of why in spite of the electron donor–acceptor binary systems studied do intermediate nematic phases appear. This effect can be due to the fact that the smectic A phases, of the components are of different type. According to the X-ray investigations the smectic A phase of the 4-nitrophenyl 4-*n*-alkyloxybenzoates is a smectic A_d phase because the ratio of the layer spacing d and the molecule length L is 1·15 [32].

The smectic A phase of 4-octylamino 4′-bromobiphenyl is a monolayer smectic phase ($d/L = 0{\cdot}9$). If in mixtures of such components the ratio of the layer spacings is sufficiently high the S_{A_d} and the monolayer smectic A phase of both components can be separated by a nematic region [33, 34].

The same reason can possibly be discussed in the diagram of *n*-undecyl 4[4-ethoxybenzylideneamino]-α-methylcinnamate (figure 5) because for the smectic A phase of this terminal non-polar compound the ratio d/L is somewhat greater than 1 (1·05). On the other hand, as recently shown by Dowell [35] on the basis of a molecular lattice theory for the appearance of smectic phases, the steric situation plays an important role. It seems to be possible that the incorporation of molecules with different molecular lengths within the smectic layers can lead to the lowering of the smectic order so that for special conditions the nematic phase is stabilized in binary systems of smectogenic components.

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