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Binary mixtures of smectic A_1 s with abnormal behaviour

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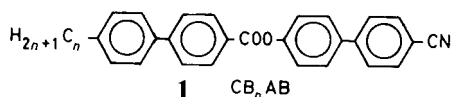
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Binary mixtures are composed of compounds belonging to the 4'-cyanobiphenyl-4-yl 4'-*n*-alkylbiphenyl-4 carboxylate homologous series and halogenophenyl 4-(trans-4-*n*-decylcyclohexyl)benzoate (10XPCHB) have been studied. Compounds CB_nAB are smectic A_1 for $n \leq 7$ and smectic A_d for $n \geq 8$; compounds 10XPCHB are smectic A_1 only. It was found that the S_{A_d} phase of compounds CB_nAB exhibits ideal miscibility with the S_{A_1} phase of compounds 10XPCHB, and that the S_{A_1} phases of both compounds show abnormal behaviour. The S_{A_1} phase of compounds CB_nAB is destabilized and the range of the S_{A_1} phase is enhanced on the side of 10XPCHB. The reasons for this behaviour are discussed.

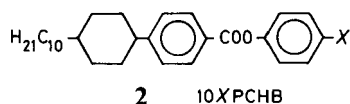
1. Introduction

It has been observed in binary mixtures of polar compounds possessing a smectic A phase that the nematic phase is created or the range of the latter phase is extended at the cost of the smectic phase if the components differ significantly in their smectic layer spacing [1-5]. This is true of mixtures composed of smectic A_1 and A_d [1-3], as well as of mixtures composed of smectic A_1 and A_1 [4, 5] or A_d and A_d [6]. If the smectic layer spacings of the components of such mixtures differ significantly, a complete separation of the smectic phases by a nematic gap may even take place. The nematic gap is not observed at a definite smectic layer spacing ratio but at various values of that ratio depending on the smectic lattice energy and chemical structure of the compounds.

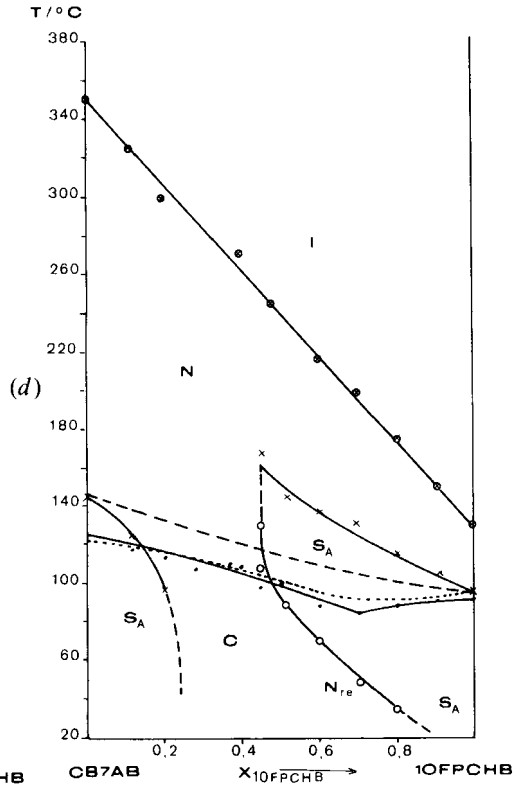
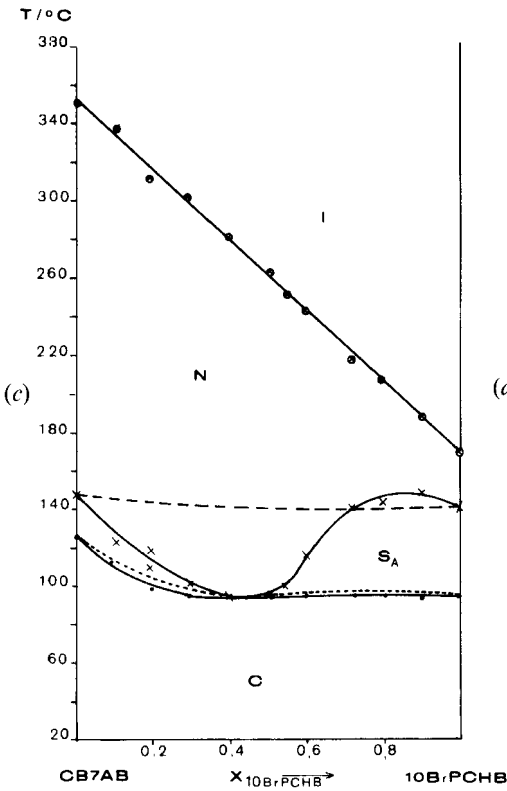
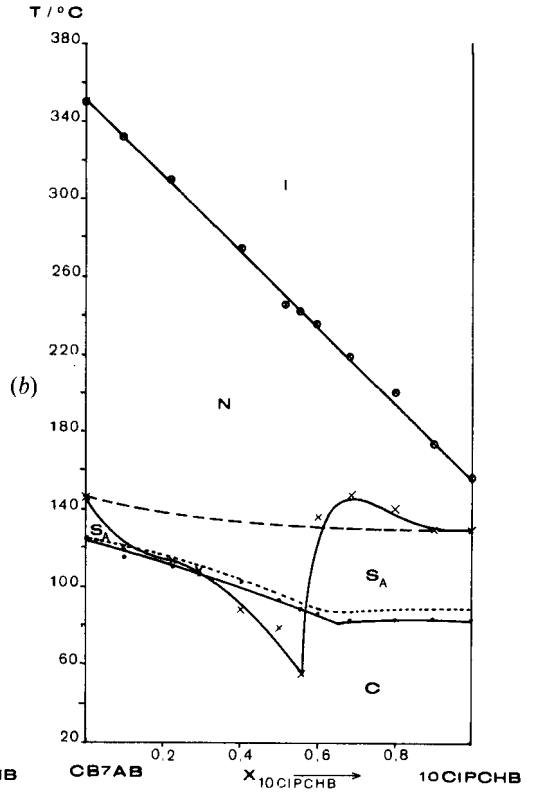
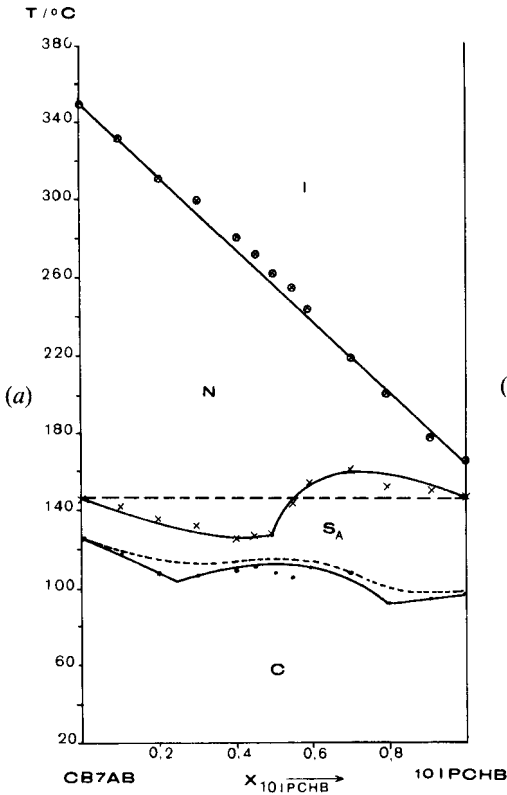
Unexpectedly it was found that similar phase diagrams may be obtained for a mixture of two different compounds with the smectic phase A_1 which have almost identical smectic layer spacings. Such behaviour was observed in some mixtures of a compound belonging to the 4'-cyanobiphenyl-4-yl 4'-*n*-alkylbiphenyl-4 carboxylate homologous series, **1**



and a compound belonging to the halogenophenyl 4-(trans-4-*n*-decylcyclohexyl)benzoate series, **2**.



In the present work phase diagrams of binary mixtures of compounds **1** and **2** are described together with a tentative interpretation of the observed anomalous behaviour due to the specific properties of the smectic phase A_1 of compounds belonging to the homologous series, **1**.



2. Experimental

Compounds **1** and **2** were obtained from Professor R. Dąbrowski and their synthesis is described elsewhere [7, 8]. Compounds **1** are smectic A_1 for $n = 5, 6$ and 7 , and smectic A_d for $n = 8$ and 9 [9]. Compounds **2** are only smectic A_1 [10].

The following series of binary mixtures were studied:

Series I: CB7AB and 10XPCHB with $X = F, Cl, Br, I$.

Series II: CB n AB and 10FPCHB with $n = 5, 6, 7$ and 8 .

Series III: CB n AB and 10IPCHB with $n = 5, 6, 7$ and 8 .

The binary mixtures were prepared by weighing out the pure compounds in proper proportions. To facilitate the formation of homogeneous samples the weighed portions were dissolved in chloroform which was subsequently evaporated. The phase diagrams of all the binary mixtures were determined by the thermo-optical method making use of the VEB Analytik Dresden polarization microscope with a heated stage. The phase transitions were determined in the heating and cooling cycles; the heating rate in the vicinity of the transition was $0.5^\circ\text{C min}^{-1}$. The phase transitions taking place below the crystallization point were observed by placing the sample on the stage, which had been heated to a temperature close to the expected transition point. The sample had in turn been heated to a temperature somewhat above the melting point by means of an additional heater. Some of the binary mixtures, viz. systems from series I with CB7AB and 10XPCHB where X was F, Cl, Br and I, were investigated by the calorimetric method using a Perkin Elmer DSC 2. The measurements were conducted in pure argon, and the heating rate was $10^\circ\text{C min}^{-1}$.

3. Results

Figures 1(a) and (d) show the phase diagrams for binary mixtures of CB7AB with 10XPCHB determined by the thermo-optical method. In all the mixtures examined a lowering of the smectic phase stability was observed when CB7AB was the excess component. The $S_A \rightarrow N$ phase transitions show a negative deviation from the theoretical line (cf. the dashed line in figures 1(a) to (d)) already at small 10XPCHB concentrations. The size of the halogen substituent in 10XPCHB was found to have a distinct effect on the stability of the smectic A_1 phase of CB7AB. The observed minimum is the smallest for the equimolar CB7AB–10IPCHB mixture and its depth amounts to 18°C . For the system with the bromo derivative the depth of the minimum increases to 53°C . In the CB7AB–10CIPCHB mixture in which the mole fraction of 10CIPCHB is 0.55, the smectic phase could be observed only after a significant supercooling of the sample below the melting point. The decrease of the smectic phase stability is greatest in mixtures of CB7AB and 10FPCHB. In the interval of 10FPCHB mole fractions from 0.27 to 0.45 the smectic phase was not observed even after supercooling the sample to 20°C .

The opposite behaviour, i.e. increase of the $S_{A_1} \rightarrow N$ phase transition temperature, is observed on the side of the 10XPCHB component. On the phase diagram a positive deviation from the theoretical line was observed. The increase of the $S_{A_1} \rightarrow N$ transition temperature depends also on the kind of halogen substituent. It is comparatively small for $X = I, Br$ or Cl and manifests itself by a small maximum of about 15°C in

Figure 1. Phase diagrams of binary mixtures for the series I CB7AB–10XPCHB: (a) $X = I$; (b) $X = Br$; (c) $X = Cl$; (d) $X = F$. The dotted line represents the liquidus curve obtained by the calorimetric method. The dashed line represents the theoretical $S_{A_1} \rightarrow N$ transition temperatures for an ideal solution calculated from the CSL equation [11].

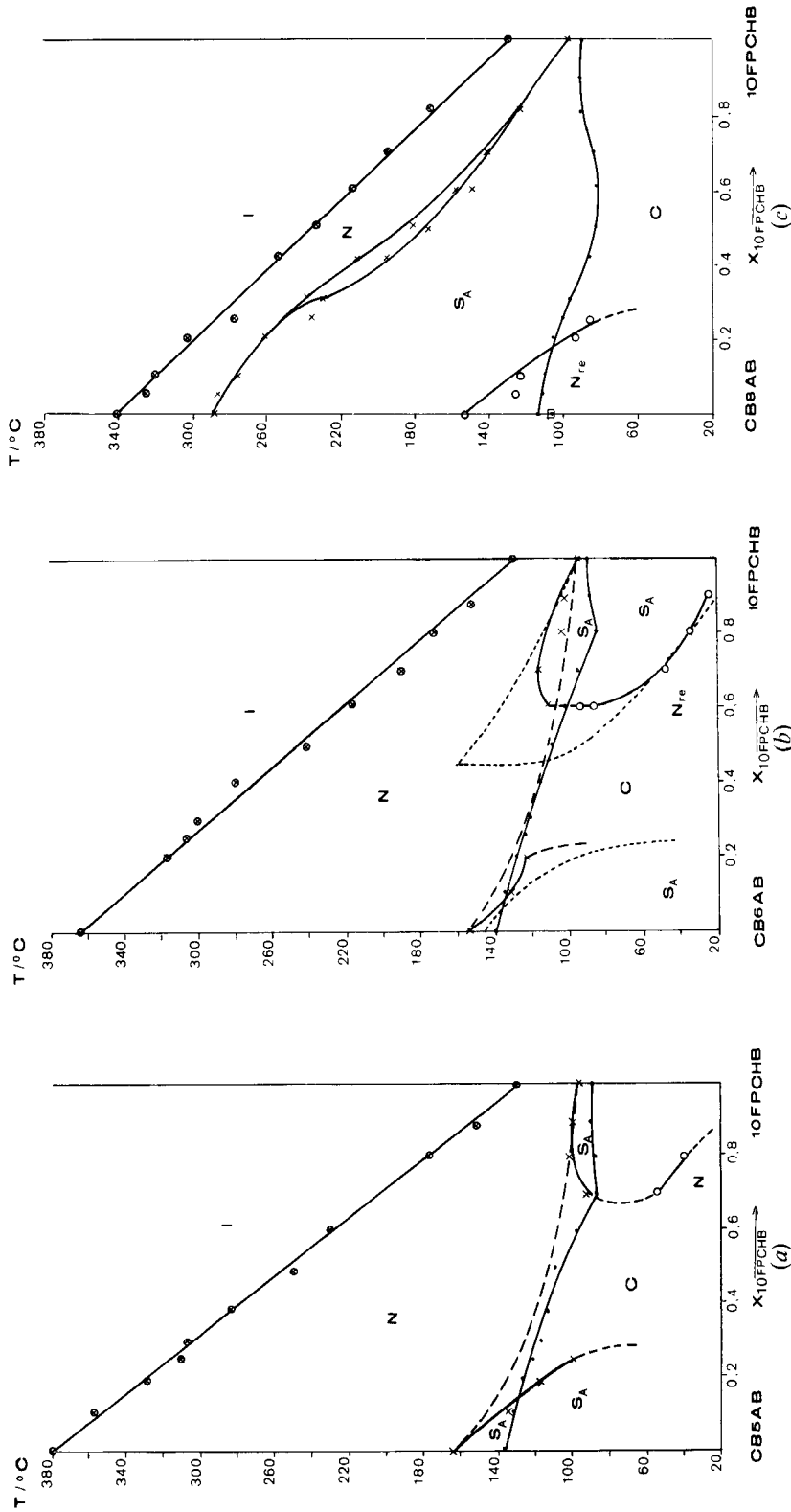


Figure 2. Phase diagrams of binary mixtures for the series II CBnAB-10FPCnB: (a) $n = 5$; (b) $n = 6$; (c) $n = 8$. The dotted line in (b) represents the $S_{A_1} \rightarrow N$ transition temperatures for the CB7AB-10FPC7B system. The dashed lines in (a) and (b) represent the theoretical $S_{A_1} \rightarrow N$ transition temperatures for an ideal solution calculated from the CSL equation [11].

mixtures containing 0.7 mole fraction of the 10XPCHB component. In contrast, for the mixture of CB7AB and 10FPCHB a significant increase of the $S_A \rightarrow N$ phase transition was observed, reaching about 60°C for a mole fraction of 10FPCHB of 0.45. In addition to the increase of the $S_A \rightarrow N$ phase transition temperature, the presence of the nematic phase below the smectic phase was observed during cooling mixtures of CB7AB and 10FPCHB with mole fractions of the latter ranging from 0.55 to 0.80.

For this series of binary systems calorimetric measurements have been performed. The character of the liquidus curves determined calorimetrically (cf. the dotted lines in figures 1(a)–(d)) is in agreement with the curves obtained from the thermo-optical measurements. The CB7AB–10FPCHB system exhibits a simple eutectic and both branches of the liquidus curve are in good agreement with the Le Chatelier–Schroder–van Laar equation [11], except for the region neighbouring the eutectic point. The systems with $X = \text{Br}$ or Cl reveal unlimited solubility in the solid phase and show a minimum of the liquidus curve. In the plot only the liquidus curve is shown.

The phase diagram of the CE7AB–10IPCHB system reveals a maximum and two eutectic points; this indicates the formation of a molecular compound of these two components. Similar behaviour in other systems with an iodo derivative (5IPCHB) has been observed [1]. It seems that formation of a molecular compound is typical when one of the components is an iodo derivative.

In figures 2(a) to (c) phase diagrams are presented of CB_nAB –10FPCHB mixtures with $n = 5, 6$ and 8 , obtained from thermo-optical studies. The character of these phase diagrams is similar to those for the CB7AB–10FPCHB system if the component CB_nAB shows only the smectic A_1 phase, i.e. for $n = 5$ (cf. figures 2(a)) and $n = 6$ (cf. figure 2(b)). From the data it can be concluded that the stability of the smectic A_1 phase increases with the shortening of the alkyl chain in CB_nAB components; at the same time the nematic gap widens and is shifted towards greater concentrations of the component 10FPCHB. On the side of component 10FPCHB we observe, as a result of adding CB_nAB with $n = 6$ or 5 alkyl chains, an increase in the $S_A \rightarrow N$ phase transition temperature as observed for the CB7AB–10FPCHB system. This increase is smaller the shorter the aliphatic chain. The increase of the $S_A \rightarrow N$ transition temperature is accompanied by the creation of the nematic phase below the smectic phase as for the CB7AB–10FPCHB system.

The phase diagram of the CB8AB–10FPCHB system is quite different (cf. figure 2(c)). The smectic A_d phase of compound CB8AB is completely miscible with the smectic A_1 phase of compound 10FPCHB, while the low temperature smectic A_1 phase of compound CB8AB is not observed in the mixture with 0.05 mole fraction of 10FPCHB. This is in agreement with the relationship between the stability of the smectic A_1 phase of compounds CB_nAB in the mixtures with the fluorine derivative and the length of the alkyl chain, n .

In figures 3(a)–(c) phase diagrams are shown of CB_nAB –10IPCHB systems with $n = 5, 6$ and 8 . The character of the phase diagrams is similar for the CB_nAB –10IPCHB systems when $n = 5, 6$ and 7 . In these systems we observe complete miscibility of the S_{A_1} phases of both components, though a minimum occurs on the $S_{A_1} \rightarrow N$ transition temperature on the side of component CB_nAB . In contrast to systems with the fluorine derivative, the stability of the smectic A_1 phase of component CB_nAB in the mixture decreases with shortening of the aliphatic chain. The observed minimum is the deepest for $n = 5$. It was found that in the CB8AB–10IPCHB system the miscibility of the S_{A_1} phases of both components is very good.

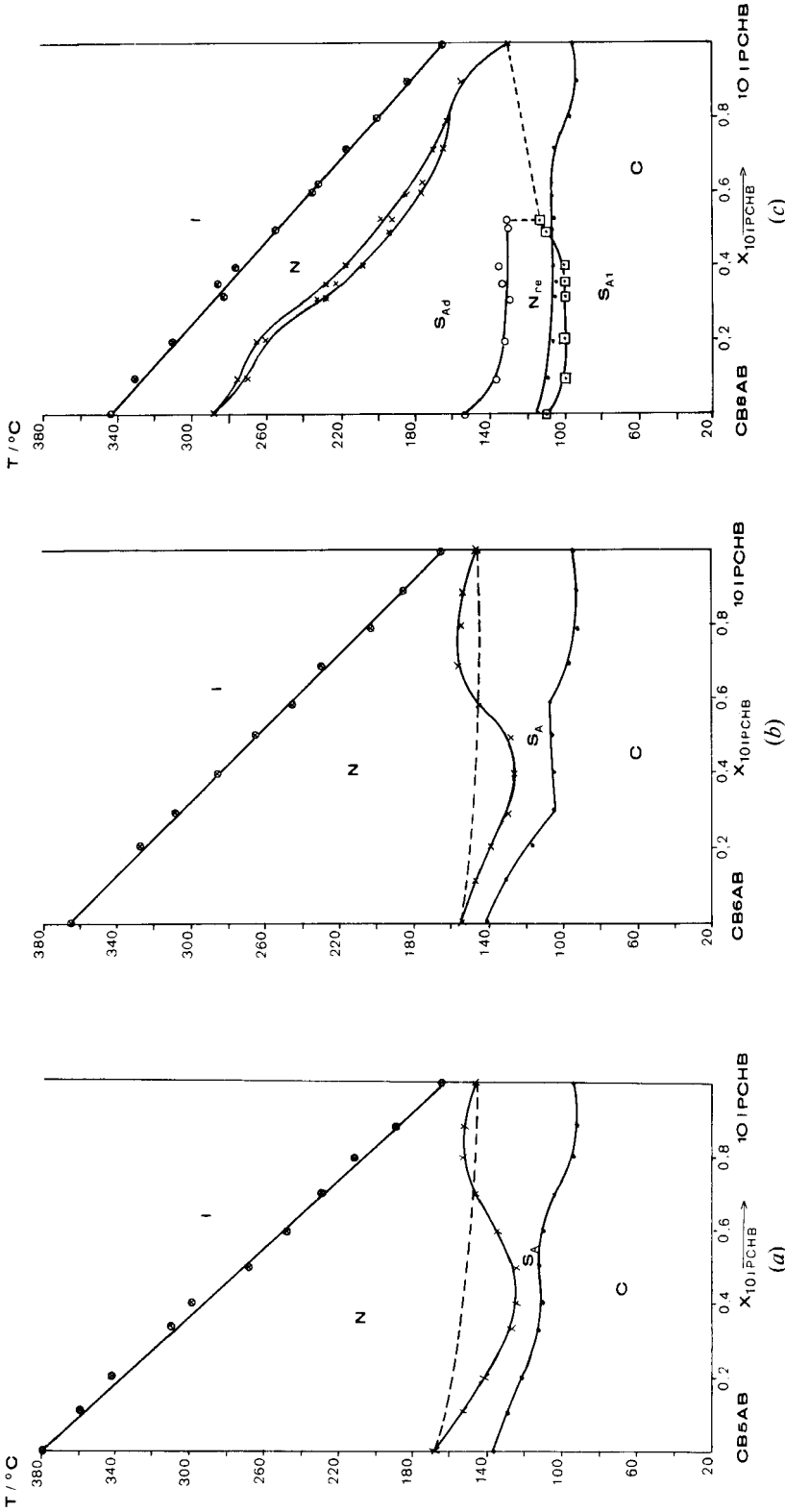


Figure 3. Phase diagram of binary mixtures for the series III $CB_nAB-10PC_nB$: (a) $n = 5$; (b) $n = 6$; (c) $n = 8$. The dashed line in (a) and (b) represents the theoretical $S_{A_1} \rightarrow N$ transition temperatures for an ideal solution calculated from the CSL equation [11]. The dotted line in (c) represents the expected $S_{A_1} \rightarrow N$ transition temperatures.

We should expect this mixture to exhibit a $S_{A_1} \rightarrow S_{A_d}$ phase transition in the 10IPCHB mole fraction range of 0.4 to 1.0 as found by Shashidhar *et al.* [12].

For the $CBnAB$ -10IPCHB systems with $n = 5, 6$ and 7 an increase of the $S_{A_1} \rightarrow N$ transition temperature is observed on the side of the latter as for systems with the fluorine derivative. However, in systems with 10IPCHB the presence of the re-entrant nematic phase was not observed.

In $CBnAB$ -10IPCHB systems with $n = 5, 6$ and 7 it was observed that the liquidus shows a maximum in the vicinity of the equimolar composition and two eutectic points. This maximum is best developed for $n = 7$ which indicates that the tendency to form molecular compounds of the components $CBnAB$ and 10IPCHB in mixtures of 1:1 composition is the greatest for systems in which the aliphatic chains of both components show the smallest differences.

4. Discussion of the results

Among the behaviour observed in the $CBnAB$ -10XPCHB systems two new interesting facts deserve particular attention. (i) In systems for which an excellent miscibility of the smectic layers should be expected due to the similar smectic layer spacing of the components (cf. $CBnAB$ -10FPCHB systems with $n = 5, 6$ and 7) the two smectic A_1 regions are separated by a nematic gap. (ii) In a mixture composed of two polar smectics A_1 the re-entrant nematic phase appears in a wide range of concentrations. So far the re-entrant nematic phase was encountered chiefly in mixtures of compounds revealing the smectic A_d phase. Pelzl [13] has observed this phase in mixtures of non-polar smectics A_1 but in a very narrow concentration interval.

In the binary $CBnAB$ -10XPCHB systems studied abnormal behaviour was observed as regards the stability of the smectic phase. In these systems we observe at the same time the destabilization of the S_{A_1} of the $CBnAB$ component and the extension of stability of the smectic A_1 phase of component 10XPCHB. Phase diagrams of similar character to those described here were found by Engelen *et al.* [14] for systems in which a nematic gap between the induced or extended smectic A_1 region and the smectic A_d region was also observed. However, the systems studied by Engelen *et al.* differ as regards their structure from those investigated here. The systems studied by Engelen *et al.* were composed of a compound without a terminal group of donor character and a compound with a terminal cyano polar group revealing the smectic A_d phase. In the systems studied here both compounds have polar molecules, and the polar groups are located in the molecules in a similar way.

We have shown that the destabilization of the smectic A_1 phase of compound $CBnAB$ in a mixture with compound 10XPCHB depends on the kind of halogen present. The stability of the A_1 phase decreases in the order $F < Cl < B < I$. It also depends on the length of the alkyl chain in compound $CBnAB$ but in a different way for the system with the fluoro and iodo derivatives. In the former case the stability of the S_{A_1} decreases more than in the latter.

The extension of the region of the smectic A_1 phase of component 10XPCHB depends also on the size of the halogen substituent and on the length of the aliphatic chain. It varies in the order $F > Cl > Br > I$ and increases with the growing length of the alkyl chain in compound $CBnAB$.

The reason for the anomalous behaviour regarding the stability of the smectic phases which we have observed is unknown. It seems that the destabilization of the

smectic A_1 phase of compounds $CBnAB$ in the mixtures is due to the partial change of ordering of the molecules in the smectic layer, i.e. the formation of dimers. This causes non-commensurability of the molecular dimensions in the layer of the mixture. It has been proved [1–4] that the incommensurability of molecular dimensions of the components making up the smectic layer is responsible for this destabilization. What are the causes of dimerization of compound $CBnAB$ in the mixture? In members of this homologous series we observe the increase of stability of the smectic A_d phase with increase in length of the alkyl chain. Compounds $CBnAB$ with $n \geq 8$ exist at higher temperatures in the form of smectics A_d and at lower temperatures as smectics A_1 ; the phases S_{A_1} and S_{A_d} are separated by a re-entrant nematic phase [9]. It can be assumed that dimerization takes place to a certain degree in members of this series with shorter alkyl chains, but the concentration of dimers is small and the smectic phase preserves the characteristic monolayer structure.

The addition of one of the compounds 10XPCHB to compound $CBnAB$ ($n \leq 7$) lowers the polarity of the system (the dielectric constants of compounds 10XPCHB are smaller than those of $CBnAB$ [15]). The lowering of the dielectric constant of the medium favours the creation of dimers. The studies of Waclawek [16] on the dimerization of PCB support this suggestion; he found that PCB in cyclohexane solution is strongly dimerized. If we assume that an increase of dimer $(CBnAB)_2$ concentration is possible in mixtures with 10XPCHB, then it will be responsible for the observed destabilization of the S_{A_1} phase of compounds $CBnAB$. It is interesting to ask, however, why phase A_1 of compound $CBnAB$ is destabilized more strongly by the fluoro derivative of 10XPCHB but less by the iodo derivative, and in the latter case why this destabilization decreases with increasing length of the alkyl chain in compounds $CBnAB$. The reason probably lies in the difference between the fluorine and iodine atoms. In the smectic layer of the $CBnAB$ –10XPCHB mixture the molecules of the compounds may be arranged in two ways: the nearest neighbour of the 10XPCHB molecule may be a second 10XPCHB molecule or a $CBnAB$ molecule. This second arrangement is more advantageous for $CBnAB$ –10IPCHB systems because of the large size of the iodine atom, as it ensures a better packing of the layer. The liquidus curves in the phase diagrams, shown in figures 1(a), 3(a) and 3(b), point to the formation of molecular compounds 10IPCHB– $CBnAB$ of composition close to 1 : 1. The 10IPCHB– $CBnAB$ intermolecular forces are the stronger the greater is the value of n in $CBnAB$. In view of the formation of intermolecular compounds the tendency of $CBnAB$ to dimerize is weakened. Thus the destabilization of the S_{A_1} phase of compounds $CBnAB$ in the mixture with 10IPCHB is small and decreases with growing n . In mixtures of $CBnAB$, with the fluoro derivative of 10XPCHB, the interaction between the compounds of the same kind is probably preferred, so the tendency of $CBnAB$ to dimerize increases, resulting in strong distortion of the smectic A_1 lattice.

The observed extension of the smectic A_1 region on the side of excess of the 10XPCHB component in the phase diagrams may be explained as follows. Probably the introduction of the $CBnAB$ molecules ($n = 7, 6, 5$) into 10XPCHB results in the formation of dimers, in this matrix with its much lower dielectric constant. Hence the $S_{A_1} \rightarrow N$ transition temperature of the mixture changes as for a compound with a virtual transition $S_{A_d} \rightarrow N$ (component $CBnAB$) and enantiotropic transition $S_{A_1} \rightarrow N$ (component 10XPCHB). By extrapolating the $S_{A_1} \rightarrow N$ transition line to a mole fraction of 10FPCHB equal to zero (figures 1(d), 2(a) and 2(b)) we can determine the $S_{A_1} \rightarrow N$ virtual transition temperature for the pure $CBnAB$ component. For $n = 5$,

6 and 7 they are 135°C, 160°C and 230°C, respectively. The S_{A_d} phase of the $CBnAB$ compounds mixes with the S_{A_1} phase of the $10XPCHB$ compounds, as is seen in the $CB8AB-10XPCHB$ phase diagrams for $x = F$ and I . As the concentration of $CBnAB$ in the mixture increases the polarity of the mixture becomes greater. Hence ever smaller numbers of $CBnAB$ molecules dimerize. At a certain concentration the ratio of dimers and single molecules is such that the smectic lattice is strongly disturbed. This is reflected by the lowering of the $S_{A_1} \rightarrow N$ phase transition or the creation of the nematic gap. The appearance of the re-entrant nematic phase on the right-hand side of the diagrams in figures 1(d), 2(a) and 2(b) may also be explained by the change of the dimer to monomer ratio under the influence of changing temperature.

These explanations are largely hypothetical. Their confirmation requires additional research in which dielectric and X-ray studies seems most promising as they should reveal the changes in the state of association of the molecules. Such research is under way and the results will be presented in the near future.

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