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Induction of smectic A_d phase in polar systems
I. Mixtures of *n*CBB and *n*OCB

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Bicomponent mixtures of 4-cyanobiphenyl-4′-yl 4′-alkylbiphenyl-4-carboxylates (*n*CBB) and 4-alkoxy-4′-cyanobiphenyls (*n*OCB) were studied and their phase diagrams obtained by thermomicroscopy. The strong enhancement of a smectic A_d phase in mixtures with the smectic members of the *n*OCB ($n \geqslant 8$) series and the induction of a smectic A_d phase in the shape of an island surrounded by a nematic phase in mixtures with the nematic members of the *n*OCB ($n < 8$) series were observed. The influence of aliphatic chain length on the observed phenomena is discussed.

1. Introduction

The nematic re-entrant phase N_{re} was observed for the first time in 1975. It appeared in a mixture of 4-cyanobenzylidene-4′-octyloxyaniline (CBOOA), exhibiting a nematic phase, and 4-hexyloxybenzylidene-4′-aminobenzontrile (HBAB), exhibiting a nematic and a smectic A_d phase [1]. Below a more ordered smectic A_d phase, a less ordered nematic phase therefore occurred. The results of experiments and the theoretical explanation of the re-entrant phenomenon in liquid crystals have been discussed in the literature many times [2–10]. X-ray measurements confirm that in all cases the nematic re-entrant phase in polar compounds appears below a smectic A_d phase, which is characterized by a thickness of the smectic layers d, such that $l < d < 2l$, where l denotes the length of the molecule.

The re-entrant phenomenon in mixtures and in pure compounds is due to the change in an equilibrium between associated and non-associated forms of the molecules (monomer$\rightleftharpoons$dimer$\rightleftharpoons$trimer) as a result of a change in temperature and the competition between short and long range order.

The re-entrant nematic phase occurs for pure compounds with terminal groups such as $-NO_2$ or $-CN$ and belonging to three ring homologous series in which members with short aliphatic chains exhibit a nematic or a nematic and smectic A_1 phase and members with longer aliphatic chains also exhibit a smectic A_d phase [11]. It occurs also for mixtures of two ring compounds belonging to homologous series with similar behaviour, chosen in such a way that a member with a nematic phase is mixed with a member with a smectic A_d phase [12]. In the latter systems, the N_{re} phase appears over short concentration and temperature ranges. The smectic A_d phase vanishes rapidly in such mixtures when the content of the nematic component increases. The area of the smectic A_d phase in the phase diagram is of a parabolic shape. The widest concentration range of a N_{re} phase is usually obtained when the first member with a smectic A_d phase is mixed with the nearest nematic member.

We have found new systems for which the re-entrant nematic phase exists over a very large concentration range and a smectic A_d phase occurs in the shape of an elliptical island surrounded by a nematic sea. These systems are created by mixing only two polar nematic compounds. In this paper we show that a continuous transformation from systems with a strong enhancement of the smectic A_d phase to systems with an induced smectic A_d phase is possible.

Ważyńska [13] and Dąbrowski [14] previously found that in some mixtures of polar compounds in which the first component is chosen from the *n*CBB or *n*OBCAB homologous series (members without the smectic A_d phase, $n < 7$ and $n < 8$, respectively) and the second one is a three ring compound, with polar ($-NO_2$, $-CN$) or intermediately polar ($-NCS$, $-COCH_3$, $-F$) group, having a smectic A_d or A_{1e} phase ($n > 7$) there occurs, besides a nematic gap, also the N_{re} phase and enhancement of the smectic phases. When the second compound has a shorter alkyl tail ($n < 7$), the smectic A phases of both components are miscible and give a continuous region of smectic A phase. X-ray investigations confirmed that smectic A_d

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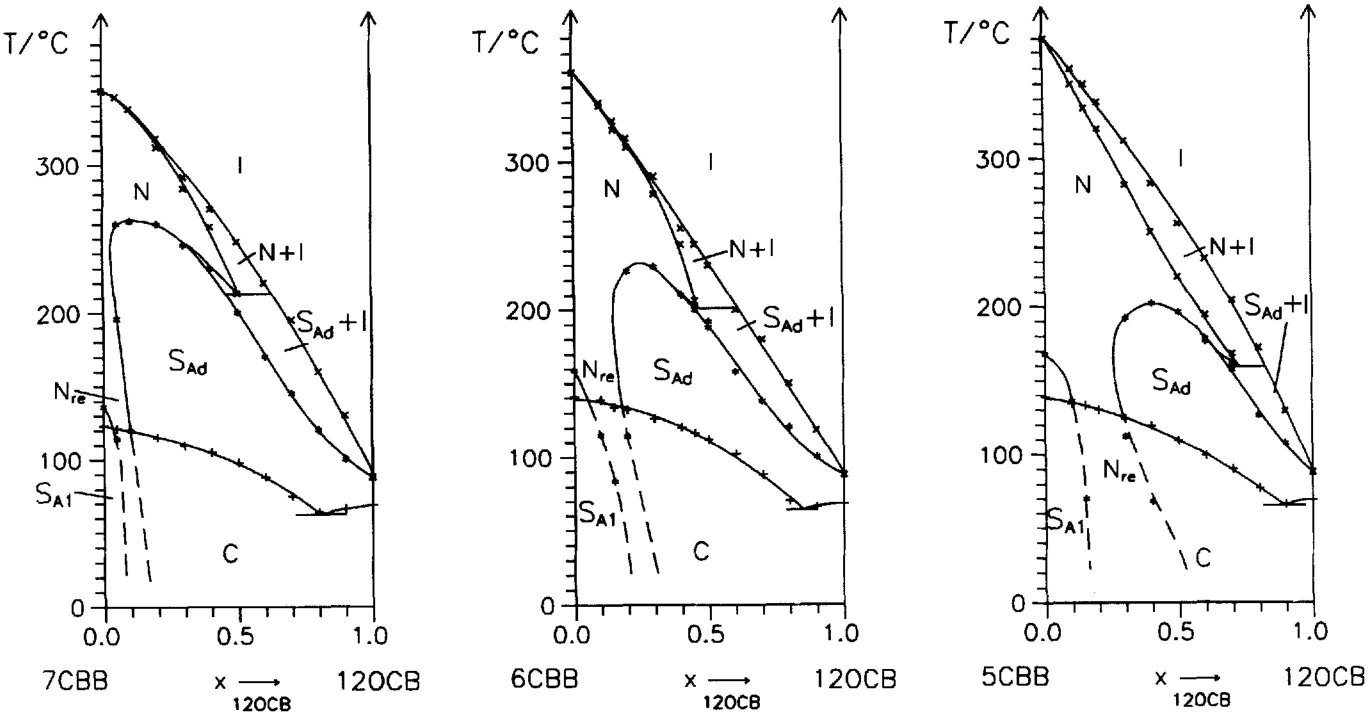


(a) (b) (c)

Figure 1. Phase diagrams of bicomponent mixtures: (a) 7CBB–12OCB, (b) 6CBB–12OCB and (c) 5CBB–12OCB.

phase occurs in the enhanced smectic A phase region, and even in the smectic $\mathrm{A_{1e}}$ host [15].

When *n*CBB compounds (members without smectic $\mathrm{A_d}$ phases) were mixed with two ring *n*OCB compounds, we observed that for the smectic $\mathrm{A_d}$ members of the *n*OCB series, a strong enhancement of the smectic $\mathrm{A_d}$ phases occurs and that for members having only the nematic phase, the smectic $\mathrm{A_d}$ phase appears in the shape of an island, surrounded by nematic phase.

We present our results concerning the induction of the smectic $\mathrm{A_d}$ phase in the shape of an island, and give an explanation for such phenomena.

2. Experimental

The compounds investigated have the following structures:

(*n*CBB)

with $n = 7, 6, 5$ [16], and

(*n*OCB)

with $n = 12, 10, 8, 7, 6, 5, 4$ [17].

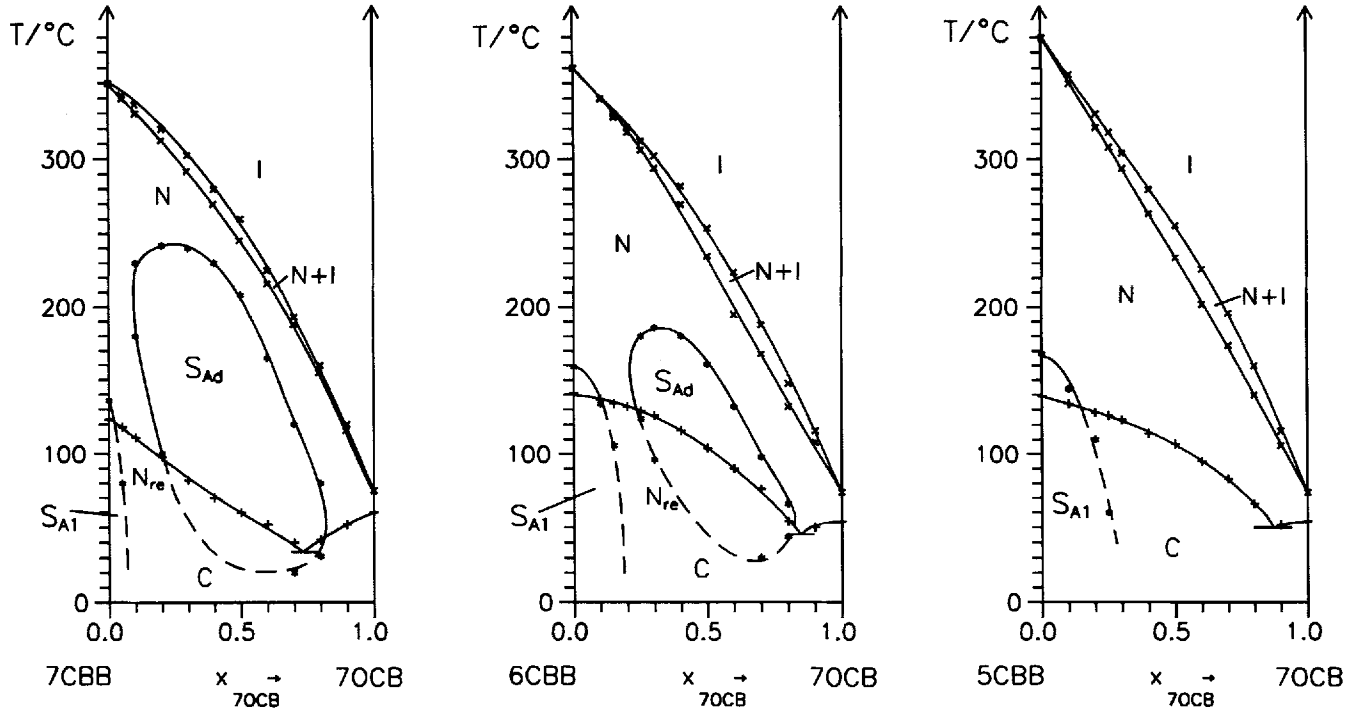
The *n*CBB compounds belong to a homologous series in which members with longer alkyl chains ($n > 7$) possess a smectic $\mathrm{A_d}$ and a $\mathrm{N_{re}}$ phase, and members with shorter alkyl chains possess a nematic and a smectic $\mathrm{A_1}$ phase.

The *n*OCB compounds have a smectic $\mathrm{A_d}$ phase when $n > 7$ and a nematic phase when $n \leqslant 7$. The compounds were synthesized and purified in our laboratory—the *n*CBB compounds according to the method described in [16] and the *n*OCB compounds by alkylation of 4-hydroxy-4′-cyanobiphenyl. Their phase transitions were concordant with those described by Gray [17]

The phase transition temperatures of the pure compounds and their mixtures were measured by thermomicroscopy using a polarizing microscope (BIOLAR) and a hot stage unit (Linkam TMS 91). In the region of a phase transition, the heating ratio was $1°\mathrm{C\,min^{-1}}$. The phase diagrams for several binary mixtures are shown in figures 1, 2 and 3, where the phase transition temperatures are plotted against molar concentration. Biphasic areas existing over a range of $\leqslant 1°\mathrm{C}$ are not indicated.

3. Results and discussion

In figure 1 (a) the phase diagram of the 7CBB–12OCB system is shown. It is seen that the smectic $\mathrm{A_1}$ and $\mathrm{A_d}$ phases of the two components do not mix and their areas of existence are separated by a nematic gap. The smectic $\mathrm{A_1}$ phase from the 7CBB side is suppressed and the smectic $\mathrm{A_d}$ from the 12OCB side is enhanced strongly. The nematic re-entrant phase appears over a short concen-



(*a*) (*b*) (*c*)

Figure 2. Phase diagrams of bicomponent mixtures: (*a*) 7CBB–7OCB, (*b*) 6CBB–7OCB *and* (*c*) 5CBB–7OCB.

tration range. In this system, the smectic A_d phase exists up to 264°C, while for pure 12OCB, it exists only up to 88·5°C. This indicates the strong virtual tendency of 7CBB to form a smectic A_d phase in the mixtures. Similar phase diagrams were also observed for the systems 7CBB–10OCB and 7CBB–8OCB—see figure 4.

In figures 1 (*b*) and (*c*) the enhancement of the smectic A_d phase for the pairs of compounds 6CBB–12OCB and 5CBB–12OCB, which show similar features to those described above, is illustrated. The alkyl chain length of the *n*CBB component influences the area of the smectic A_d phase, this region of smectic A_d phase becoming smaller when the alkyl chain is shorter (see figure 1 (*c*), 5CBB–12OCB).

In figure 2 (*a*), the phase diagram for 7CBB–7OCB is presented. None of these compounds has a smectic A_d phase, but this phase occurs in their mixtures. The existence area of the smectic A_d phase appears in the shape of an island surrounded by nematic phase. On the side of low temperatures, the smectic A_d phase exists below the melting point, and the monotropic N_{re}–A_d phase transition temperatures are impossible to observe over the entire concentration range because of crystallization of 7CBB from these mixtures. The smectic A_1 region does not join the area of the induced A_d phase, as in the systems described above. The tendency of the compound 7CBB to form the smectic A_d phase in this mixture is very strong; it exists up to 260°C and the temperature range is 200°C. For shorter *n*CBB members, the tendency to create the smectic A_d phase is weaker—see figure 2 (*b*) for 6CBB–7OCB, and the phase does not occur when the aliphatic chain is too short—see the 5CBB–7OCB system in figure 2 (*c*). In the case of 6CBB–7OCB, it was still impossible to supercool the mixtures and measure the monotropic N_{re}–A_d transition temperatures over the entire concentration range.

It is seen that the decreasing tendency for induction of a smectic A_d phase is accompanied by a lower suppression of the stability of the smectic A_1 phase by comparing the areas of smectic A_1 phase in figures 2 (*a*) and (*b*).

The smectic A_d is also less effectively enhanced when the alkyl chain length of *n*OCB shortens—see figure 3, and as this occurs, the smectic A_d island shrinks and disappears. In the system 7CBB–*n*OCB, the smectic A_d phase is not injected for $n \leqslant 3$; this is also the case in the system 6CBB–*n*OCB for $n \leqslant 5$.

Phase diagrams, shown in figures 2 (*a*), (*b*), 3 (*a*), (*b*) and (*c*), relate to mixtures of nematic compounds in which the induction of a smectic A_d phase appears. No such bicomponent polar system has yet been described in the literature. The smectic island of a smectic A_d phase surrounded by a nematic sea was observed by Illian *et al.* [18], in the tricomponent mixture composed of two polar compounds (4-cyanobenzylidene-4′-octyloxyaniline

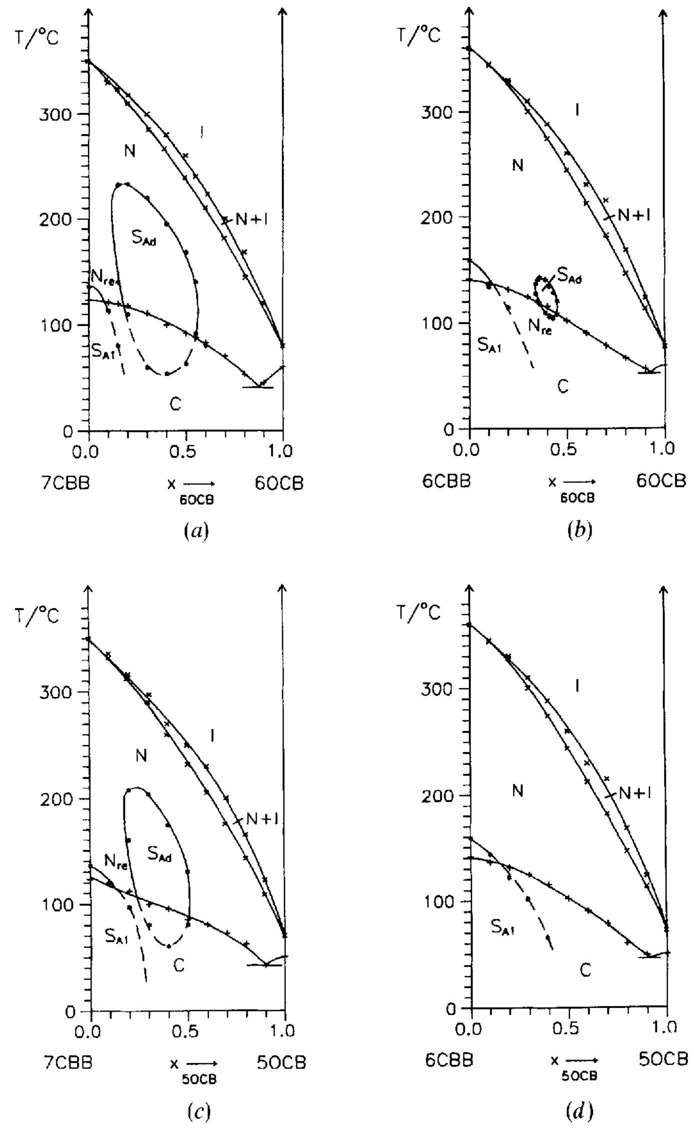


Figure 3. Phase diagrams of bicomponent mixtures: (*a*) 7CBB–6OCB, (*b*) 6CBB–6OCB, (*c*) 7CBB–5OCB, and (*d*) 6CBB–5OCB.

(CBOOA) and 4-heptyloxy-4′-cyanobiphenyl (7OCB)) and the non-polar ester (4-pentylphenyl 4-octyloxybenzoate (8.O.5)). In this mixture one nematic component is the compound 7OCB and the other one is a mixture of CBOOA and 8.O.5 chosen from the concentration range where a nematic gap occurs between the smectic A_d phase and the induced smectic A_1 phase in the phase diagram. This bicomponent nematic phase is created by suppressing the stability of the smectic A_d phase of CBOOA. After introducing the polar compound 7OCB into such a mixture, the concentration of the non-polar ester 8.O.5 is decreased and the destabilization of the smectic A_d phase of CBOOA is cancelled.

In the case of our systems, the mechanism of induction of the smectic A_d phase is different. None of the compounds has a smectic A_d phase. The induction is due to specific features of the *n*CBB compound. Such a conclusion may be drawn if we compare the change in area of the smectic A_d phase with change in the alkyl chain length of the *n*OCB component in the system 7CBB–*n*OCB—see figure 4.

The enhancement of the smectic A_d phase observed for mixtures with 12OCB, 10OCB and 8OCB and the injection of a smectic A_d phase observed for mixtures with 7OCB, 6OCB, 5OCB and 4OCB arise for the same reason—the appearance of long range antiferroelectric order of the smectic A_d type. In the case when the *n*OCB compound has a nematic phase ($n \leqslant 7$), the induced smectic phase can exist in the shape of an elliptical island. For members which exhibit smectic phases ($n > 7$), the area of the induced smectic A_d phase joins the smectic A_d phase of the *n*OCB compound giving one common area of smectic A_d and is seen as a unified area of enhanced smectic A_d phase of the *n*OCB compound.

The formation of the induced smectic A_d phase in *n*CBB–*n*OCB systems may be explained by the mean field approximation model of Longa and de Jeu [4] or Berker's frustrated spin gas model [7–9]. In both models the role of the alkyl chain length is very important. Also, the

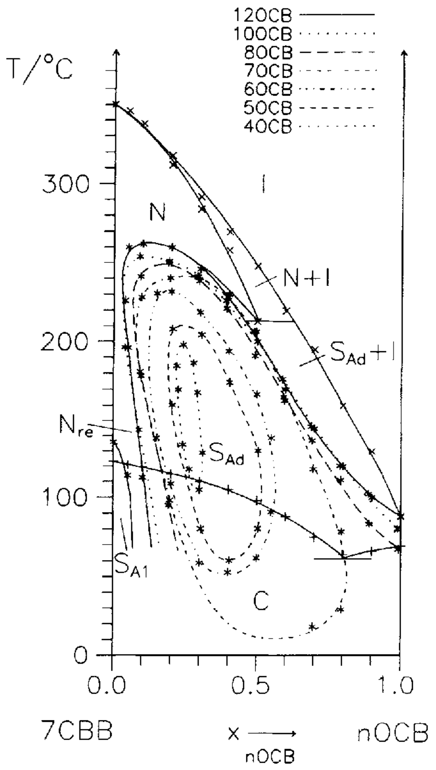


Figure 4. Phase diagram of bicomponent mixtures of 7CBB and *n*OCB.

experimental results show that there is a critical length of the alkyl chain for the appearance of the smectic A_d phase in the pure compounds of the homologous series—usually it is $n > 7$. In our case, the 6CBB–6OCB system is the one involving the shortest alkyl chain lengths for which the smectic A_d phase is still injected. However, in other works on the *n*EPCH series, the smectic A_d phase, is observed for the compound with a butyl chain [19].

The theoretical model of Longa and de Jeu postulates that both monomers and dimers are necessary to form a stable smectic A_d phase because the space is filled better than when a dimer is surrounded only by dimers. Their model and also calculations by Madhusudana [10] show that longer molecules with a terminal polar group more easily associate in an antiparallel manner forming the partially bilayer structure with $d/l \sim 1{\cdot}4$ than shorter molecules. In these models, the concentration of dimers increases with decrease in temperature. The smectic A_d phase is observed over a limited range of dimer concentrations, below and above which a smectic phase disappears. At lower temperatures, this is caused by the unfavourable packing of dimers, and at higher temperatures by a drop in their concentration and an increase in thermal disorder. In our bicomponent systems, *n*CBB–*n*OCB, three different types of associate may be present $(CBB)_2$, $(OCB)_2$ and CBB–OCB and the concentration can be expressed by the equilibria:

$$2CBB \rightleftharpoons (CBB)_2;\ 2OCB \rightleftharpoons (OCB)_2;$$

$$CBB + OCB \rightleftharpoons CBB\text{–}OCB.$$

One may suppose that dimer concentrations in the mixture of *n*CBB and *n*OCB would be higher than in pure *n*CBB, because in this mixture consisting of molecules with different lengths ($l_{7CBB} = 31{\cdot}5$ Å, $l_{8OCB} = 23{\cdot}4$ Å), steric conditions for the parallel oriented molecules are worse. X-ray investigations of a similar system, 7BCB–8.CN (4-cyanobiphenyl-4′-yl 4-heptylbenzoate and 4-cyanophenyl 4-octylbenzoate), show that the induced smectic A_d phase has a smectic layer spacing nearly equal to the length of the 7BCB dimers ($d = 33{\cdot}3$ Å for samples from the concentration range 80–30 mol% of 7BCB from the smectic A_d island, $d = 33{\cdot}5$ Å for the cybotactic groups in the nematic phase of 7BCB, and $d = 31{\cdot}6$ Å for the cybotactic groups in the nematic phase of 8.CN). On this basis, it may be concluded that $(CBB)_2$ dimers are dominating in relation to others. From X-ray investigations, we have not obtained evidence that their concentration really grows when the *n*OCB compound is introduced into the *n*CBB compound, but in the near future we will investigate dielectric, spectral and density properties of these and similar systems to learn about the nature of the dimers and the change in their concentration with temperature, composition and phase transition points.

In Berker's spin gas model, dimers and monomers do not play an important role; they are only components of trimers and, according to calculations, their concentration does not change on crossing from N–S_{A_d} or S_{A_d}–N_{re} phase [8]. In relation to a capacity for stabilizing smectic layering, associations of at least three molecules are deemed to be energetically favourable. Three molecules can form a correlated trimer with dipolar short range antiferroelectric or ferroelectric order. Molecules in these trimers occupy energetically preferred positions (notches) in the direction of the long molecular axis (z direction) and the number of these positions depends on alkyl chain length. Depending on entropy and energetic quantities, the trimers may or may not aggregate laterally to form a percolating network or molecular polymer in the xy plane. If a polymer is formed, it means that a smectic phase is created. The layer spacing and pair length in this model have a statistical character with different identities for different types of microscopic configuration. The pair potential for nearest-neighbour molecules in the trimers was calculated taking into account van der Waals forces, which favour parallel (ferroelectric) ordering of the molecules, and steric forces, which favour antiparallel (antiferroelectric) ordering. Competition between these factors is characterized by the ratio B/A; when $B/A < 1$ a steric hindrance wins, and when $B/A > 1$ van der Waals attractions win. Another important parameter is a/l, where a is the average lateral separation of a nearest neighbour pair and l is the molecular length.

According to the spin gas model, the observed induced smectic A_d phase in the *n*CBB–*n*OCB systems may be interpreted in the following way. If we assume that in the mixture *n*CBB–*n*OCB, the ratio B/A does not change, the value of the ratio a/l grows because the average value of l decreases. Such a situation promotes smectic A_d phase formation—see diagrams in figure 2 in [7]. *n*CBB and *n*OCB molecules have also different lengths of their rigid cores, so in the mixtures the steric hindrance also increases. From these two reasons it is possible to conclude that in the mixture *n*CBB–*n*OCB there are better conditions for creating a smectic A_d phase than in the pure components.

By both theoretical models, we can explain the injection of a smectic A_d phase in a mixture of polar nematic compounds. Berker's model seems to be better from the standpoint of the dielectric results related to change in $\varepsilon_\parallel$ and $\bar{\varepsilon}$ for systems with A_d and N_{re} phases [20, 21] than the model of Longa and de Jeu. For our mixtures, further experiments are necessary to choose which of the models most closely describes the system.

The widest temperature range of an induced smectic A_d phase has been observed for a large concentration of 7CBB and this implies that a small concentration of *n*OCB is enough to remove the uncomfortable condition for forming a smectic A_d phase in pure 7CBB. This compound therefore reveals its virtual smectic A_d character. The molecular structure of both compounds is however important for observation of the induction of the smectic A_d phase.

4. Conclusions

Examining the phase diagrams of bicomponent *n*CBB–*n*OCB systems shows that strong induction of a smectic A_d phase occurs. The appearance of a N_{re} phase indicates that this smectic must be a smectic A_d phase. The induction is a result of revealing the virtual smectic A_d phase character of the *n*CBB compound in such mixtures. In a subsequent paper we will demonstrate how the value of the N–S_{A_d} virtual phase transition temperature may be estimated.

The lengths of both components influence the ability to give the induction. For *n*OCB components with long alkyl chains ($n > 7$), the area of the induced smectic A_d joins the smectic A_d phase of the pure *n*OCB compound which gives rise to the enhancement of the smectic A_d phase of the *n*OCB compound. When the alkyl chain of the *n*OCB compound is shortened, the stability of the induced smectic A_d phase decreases. For the members of the *n*OCB series that do not have smectic phases ($n \leqslant 7$), the induction of the smectic A_d phase is observed, but in the form of an island surrounded by the nematic. When the alkyl chain is too short, no smectic A_d phase is injected (for example 7CBB–3OCB, 6CBB–5OCB).

When the alkyl chain of the *n*CBB compound decreases, virtual properties weaken and for 5CBB, the induction is not observed even with 7OCB. We have found that the polar systems described and for which the smectic A_d island is created are not rare examples, but exemplify a very common behaviour. Other similar systems will be reported soon. Probably the spin gas model is most consistent with the observed features of the systems investigated, but further experimental work is necessary for confirmation of this conclusion.

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