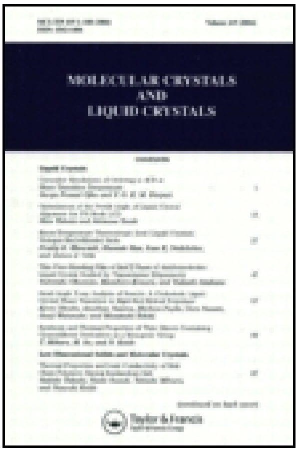

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The Influence of the Concentration of Fluoro- and Cyanoterminated Compounds on the Induction of Antiferroelectric Phase and on Helical Pitch

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The Influence of the Concentration of Fluoro- and Cyanoterminated Compounds on the Induction of Antiferroelectric Phase and on Helical Pitch

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To compare the ability of two compounds (S)-4-(1-methylheptyloxycarbonyl) phenyl 4′-(1H,1H,2H,2H perfluorooctyloxy)biphenyl-4-carboxylate and (S)-4-(1-methylheptyloxycarbonyl)phenyl 4′-(cyanometanoyloxyhexyloxy)biphenyl-4-carboxylate (shortly fluoro- and cyanoterminated compounds) for the induction of antiferroelectric phase (SmC^*_A), the mixtures of both compounds in the mole ratio 2:1, 1:1 and 1:2 were mixed with (S)-4-(1-methylheptyloxycarbonyl)biphenyl 4′-(etanoyloxypropoxy)phenyl-4-carboxylate (2H3B). The change of maximum temperature range of induced SmC^*_A phase is not linear with the concentration of cyanoterminated compound. In the basic systems comprising pure fluoro- or cyanoterminated compounds in the mixture with 2H3B the temperature characteristics of helical pitch (wavelength of selectively reflected light) are opposite. In three component mixtures it is observed the stepwise change from characteristics found for the bicomponent system with fluoroterminated component to characteristics observed for the bicomponent system with cyanoterminated component.

Keywords Helical pitch; induction of antiferroelectric phase; liquid crystals; selective light reflection

1. Introduction

The induction of antiferroelectric phase (SmC^*_A) was discovered in 2000 in mixtures of compounds differing in the polarity of terminal substituents [1]. At first it was observed in mixtures of compound 6F2Bi comprising fluoroterminated terminal chain with the homologous series of compounds comprising alkylated terminal chain nH3B [2]. Recently the induction of antiferroelectric phase has been found also in the system comprising cyanoterminated compound CNH6Bi with the same alkylated homologous series of compounds nH3B [3]. To compare the ability of fluoro- and cyanoterminated compounds for the induction phenomena, the mixtures of both polar compounds in the mole ratio 2:1, 1:1 and 1:2 were mixed with the homolog 2H3B, comprising the propanoyloxypropoxy unit in terminal chain. Here we also present the helical pitch measurements for all tested mixtures.

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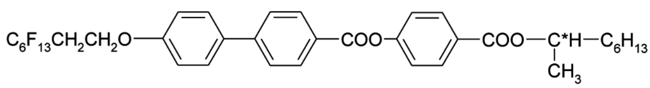
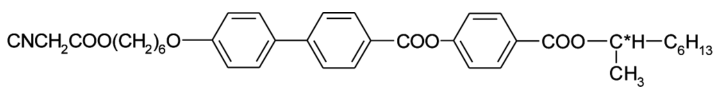
The results of measurements given in the previous paper for two separate bicomponent mixtures [4]: namely spontaneous polarization, tilt angle, layer spacing has been showed that the mechanism of induction in both cases must be slightly different.

2. Experimental Methods

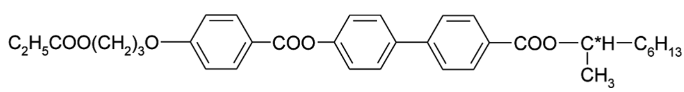
The compounds 6F2Bi and CNH6Bi as well as their mixtures in the mole ratio 2:1, 1:1 and 1:2 were mixed with the compound 2H3B.



6F2Bi Cr_1 80.7 Cr_2 98.1 SmC* 138.0 SmC^*_{α} 148.1 SmA 183.6 I [5,6].



CNH6Bi Cr 62.2 SmC* 90.5 SmA 97.6 I [7].



2H3B Cr 80.6 SmA 106.7 I [8].

Phase transitions were investigated by polarizing optical microscope (BIOLAR-PZO) connected with LINKAM – THMS-600 heating stage.

The helical pitch measurements were made based on the selective light reflection phenomenon. The measurements of light transmission were carried out on SHIMADZU UV-VIS-NIR spectrometer in the range 360–3000 nm. The tested compounds were placed on a glass plate with a CTAB layer without covering with another glass plate. A MLW U7 controller of temperature with Peltier elements was used for changing the temperature; the temperature range of measurement was 5–105°C. The temperature accuracy was 0.1°C. The presented results were obtained during the cooling cycle.

The results are presented as the wavelength of selectively reflected light λ_s versus temperature in all the figures. In order to obtain values for helical pitch, the values of λ_s should be divided by 2 and the average refractive index for the SmC* phase or by the average refractive index for the SmC^*_A phase (the value of the average refractive index for this class of materials is about 1.5 [9]).

The helical twist sense for chiral phases was determined by the method described in Ref. [10].

3. Results and Discussion

Three mixtures comprising two compounds: one with partially fluorinated group 6F2Bi and another one with cyanoterminated group CNH6Bi in the mole ratio

2:1, 1:1 and 1:2 were prepared. Their phase transition temperatures in heating cycles are as follows:

6F2Bi-CNH6Bi 2 : 1 – Cr 95 SmC* 132 SmA 141-151 I

6F2Bi-CNH6Bi 1 : 1 – Cr 90 SmC* 121 SmA 131-141 I

6F2Bi-CNH6Bi 1 : 2 – Cr 85 SmC* 115 SmA 120-126 I

These mixtures were mixed with compound 2H3B, having terminal propanoyloxypropoxy group, giving three component mixtures. Their phase diagrams are shown in Figure 1b–d, as well as the phase diagrams of bicomponent mixtures 6F2Bi-2H3B (Fig. 1a) and CNH6Bi-2H3B (Fig. 1e), already presented in [2] and [3], respectively. In all tested systems the antiferroelectric phase SmC^*_A is induced for some concentration and temperature ranges. The collection of the part of phase diagrams showing only the curves corresponding to the phase transition SmC^*_A-SmC* for five tested systems is presented in Figure 2. It shows the non linear decrease of the area of induced antiferroelectric phase towards the increase of the concentration of cyanoterminated compound. The nonlinearity is well visible when the maximum temperatures of phase transition from induced SmC^*_A to SmC* phase are compared versus the concentration of CNH6Bi, see Figure 3. The dashed line represents the linear behaviour. In the paper [4] it was shown that both bicomponent

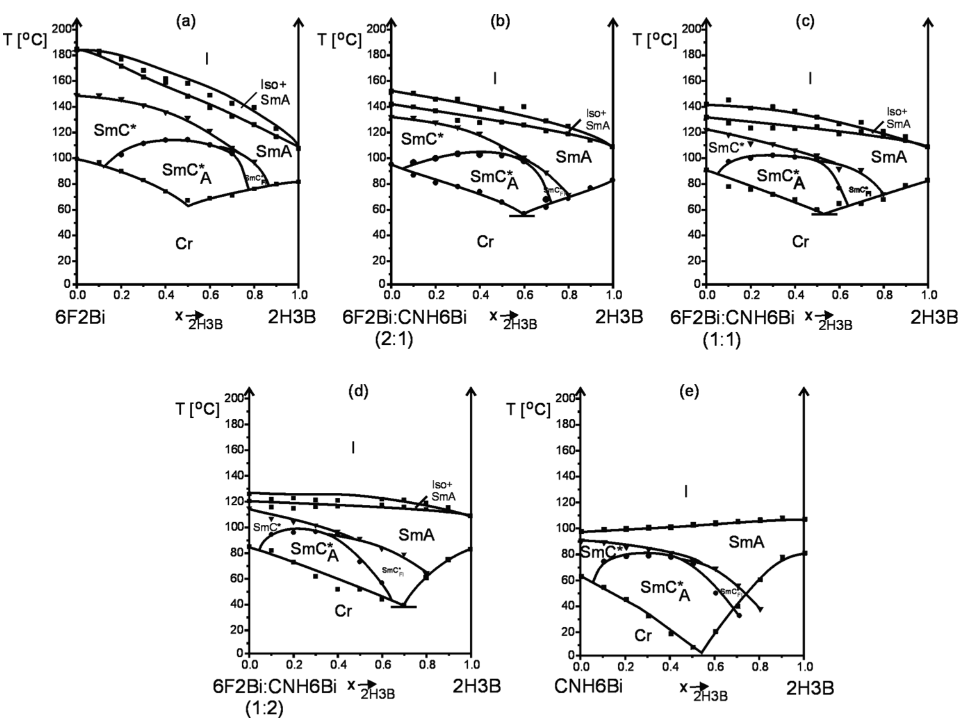


Figure 1. The phase diagrams of 6F2Bi (a), CNH6Bi (e) and their mixtures in mole ratio 2:1 (b), 1:1 (c) and 1:2 (d) with the compound 2H3B.

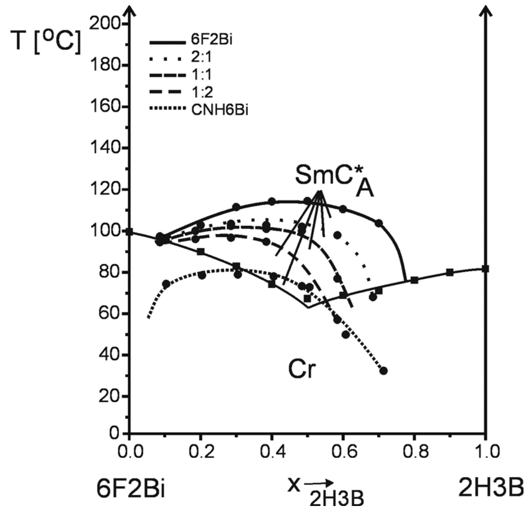


Figure 2. The phase diagram with marked regions of the existence of SmC*$_A$ phase appearing in mixtures of 6F2Bi, CNH6Bi and their mixtures in mole ratio 2:1, 1:1 and 1:2 with compound 2H3B.

mixtures comprising pure 6F2Bi and pure CNH6Bi (Fig. 1a and 1e) have different physical properties. The change of physical properties (spontaneous polarisation, tilt angle and layer spacing) upon the concentration of non-polar compound are nonlinear in the former case and linear in the latter case. The compound with fluoroalkloxy group 6F2Bi forces its ordering in mixtures. The present results of partially doped systems with cyanoterminated compound proves that the compound 6F2Bi increases induction ability of CNH6Bi.

The area of induced SmC*$_A$ phase is symmetrical in relation to 0.5 molar fraction for the system 6F2Bi-2H3B and non symmetrical for the system CNH6Bi-2H3B. The increase of the concentration of cyanocompound CNH6Bi causes the

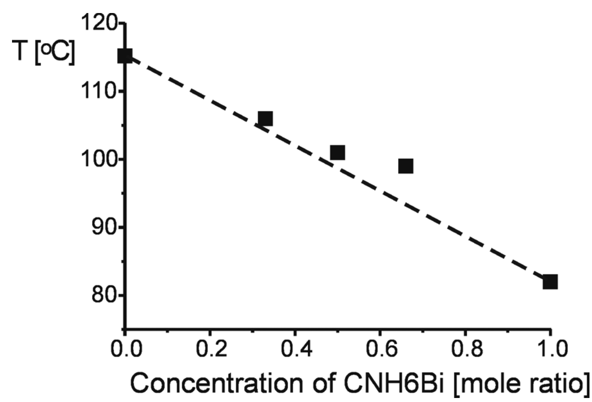


Figure 3. The maximum values of SmC*-induced SmC*$_A$ phase transition temperatures existing in mixtures of 6F2Bi, CNH6Bi and their mixtures in mole ratio 2:1, 1:1 and 1:2 with compound 2H3B; dashed line represents the linear change of temperatures of phase transition.

shift of maximum of phase transition SmC*$_A$-SmC* to the side of excess of polar component (6F2Bi-CNH6Bi mixture).

For all tested systems the measurements of the selective light reflection were performed to check how the increase of the concentration of cyanoterminated component influences on the helical pitch dependence upon temperature (Fig. 4) and concentration of alkylated compound (Fig. 5). Pure 2H3B compound does not selectively reflect the light because it has only SmA phase.

The temperature characteristics of λ_s in SmC* changes slightly. This fact inform us that also helical pitch does not change much with the change of temperature in this phase. For the mixtures of the bicomponent system 6F2Bi-2H3B (Fig. 4a) there is observed slight increase of the λ_s values with the increase of the temperature but

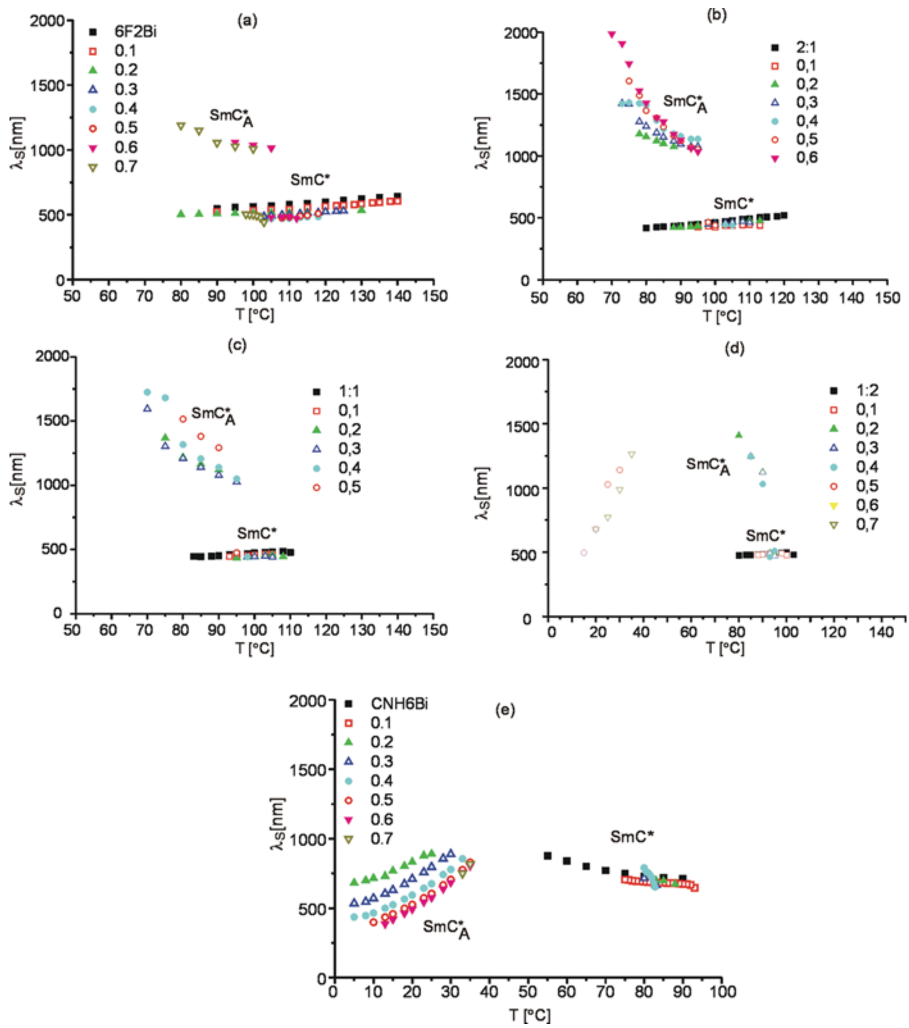


Figure 4. Wavelength of the selectively reflected light for mixtures of 2H3B with 6F2Bi (a), CNH6Bi (e) and their mixtures in mole ratio 2:1 (b), 1:1 (c) and 1:2 (d). (Figure appears in color online.)

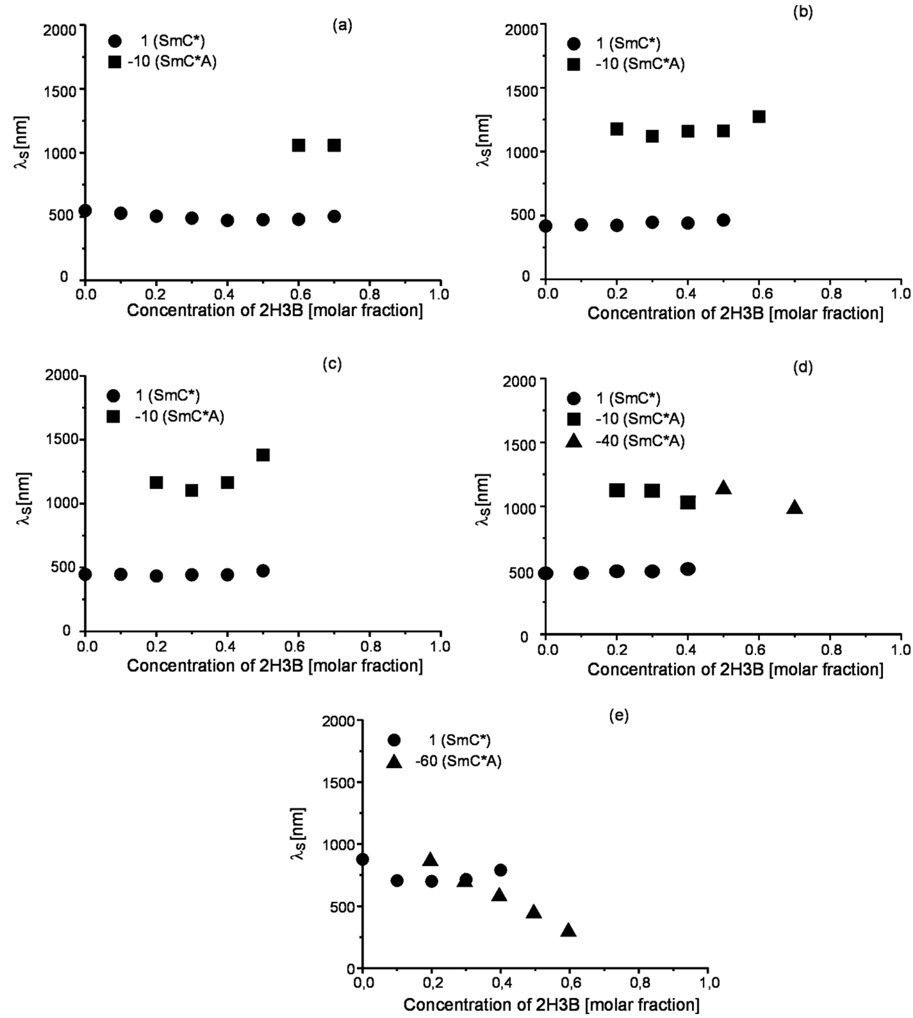


Figure 5. Wavelength of the selectively reflected light for mixtures of 2H3B with 6F2Bi (a), CNH6Bi (e) and their mixtures in mole ratio 2:1 (b), 1:1 (c) and 1:2 (d), for set temperatures in SmC* and SmC^*_A phases.

for the mixtures of the system CNH6Bi-2H3B (Fig. 4e) there is rather a decrease of values in SmC* phase. The mixtures comprising simultaneously fluoroterminated and cyanoterminated compounds with different concentration 2:1, 1:1 and 1:2 and non-polar component 2H3B (Fig. 4b-d) have these characteristics changing between both border compositions (6F2Bi-2H3B and CNH6Bi-2H3B).

In SmC^*_A phase the values of λ_s decrease for the system 6F2Bi-2H3B (Fig. 4a) and increase for the system CNH6Bi-2H3B (Fig. 4e) in a moderate way with the increase of the temperature. For the bicomponent mixtures 6F2Bi-CNH6Bi 2:1 and 1:1 doped with 2H3B (Fig. 4b, c) the strong decrease of the values of λ_s is observed with increasing temperature. For the mixture 6F2Bi-CNH6Bi 1:2 only the results of λ_s over 80°C (for concentration of 2H3B $\geq$ 0.5 molar fraction) depend the same upon temperature as for previous systems. The results for lower concentration of

2H3B (<0.5 molar fraction) appear around 40°C and strongly falls with decreasing temperature (Fig. 4d).

The measurements of helical twist sense in SmC* phase show that the helix is right-handed in all tested systems. The same measurements made in SmC^*_A phase show that the λ_s values which increase with temperature are for the right-handed helix, and the λ_s values which decrease with temperature are for the left-handed helix. For the system 6F2Bi-CNH6Bi (1:2) – 2H3B (Fig. 4d) it was observed that the Grandjean textures visible under polarized optical microscope are dark for low temperature then they are getting brighter and next they are becoming again dark with the increase of the temperature. It means that the unwinding of the helix and next its rewinding in the opposite sense with increasing temperature appear for this system. Such change of the helical twist sense within SmC^*_A phase is the same as it was observed for pure compounds of similar three ring structure [10]. For the system CNH6Bi −2H3B the microscopic observations of the textures gave the same results, thus the absence of the results of λ_s for left-handed structure in Figure 4e is because they are over measuring range of the spectrophotometer.

The comparison of the dependence of λ_s values upon the concentration of compound 2H3B with terminal alkyl chain is convenient to be shown on diagrams versus relative temperature $T\text{-}T_{C^*A\text{-}C^*}$, corresponding to the transition from the antiferroelectric to the ferroelectric phase (presented in Fig. 5). The analysis of results obtained for SmC* phase at relative temperature $T\text{-}T_{C^*A\text{-}C^*} = 1°C$, let to conclude that the increase of the concentration of alkylated compound 2H3B does not change the helical pitch in this phase, except for the bicomponent system CNH6Bi-2H3B (Fig. 5e). In this case, it is observed first the decrease and then increase of the wavelength of selectively reflected light with the increase of the concentration of 2H3B. In SmC^*_A phase the dependence of λ_s versus concentration of 2H3B is different for different systems. At higher temperature range (SmC^*_A phase presented by relative temperature $T\text{-}T_{C^*A\text{-}C^*} = -10°C$) the λ_s does not change with the concentration of 2H3B for the system comprising only 6F2Bi as well as for systems containing simultaneously 6F2Bi and CNH6Bi in the mole ratio 2:1, 1:1 and 1:2 (Fig. 5a–d – it is nearly independent upon temperature). In SmC^*_A phase at lower temperatures (at relative temperature $T\text{-}T_{C^*A\text{-}C^*} = -40°C$ or $-60°C$) the increase of the compound 2H3B causes the decrease of the helical pitch for the systems in which it is observed (6F2Bi and CNH6Bi in the ratio 1:2 with 2H3B as well as CNH6Bi-2H3B). In these two systems the mentioned dependence is near linear.

For the concentrations higher than the existence of the induced SmC^*_A phase it can be observed a SmX phase on phase diagrams, Figure 1. It is probably ferrielectric smectic C* phase (SmC^*_{FI}), because this phase is exhibited by longer homologues of 2H3B [2,8]. With the increase of the concentration of 2H3B SmC* diminishes and SmX phase appears. The maximum concentration for which the SmC* phase can be still observed can be deduced from results of selective reflection of the light in SmC* phase presented in Figure 5. For the system comprising pure 6F2Bi this maximum concentration is 0.7 molar fraction of compound 2H3B, and for system comprising pure CNH6Bi it is 0.4 molar fraction of compound 2H3B. Absence of light selective reflection results for higher concentration of 2H3B may suggest that there exist ferrielectric phase, because for MHPOBC this phase has very long pitch [11].

The increase of the concentration of CNH6Bi in the three component mixtures causes at first the decrease of the λ_s from 520 nm observed in the bicomponent system 6F2Bi-2H3B to 400 nm for bicomponent mixture 6F2Bi-CNH6Bi in the mole

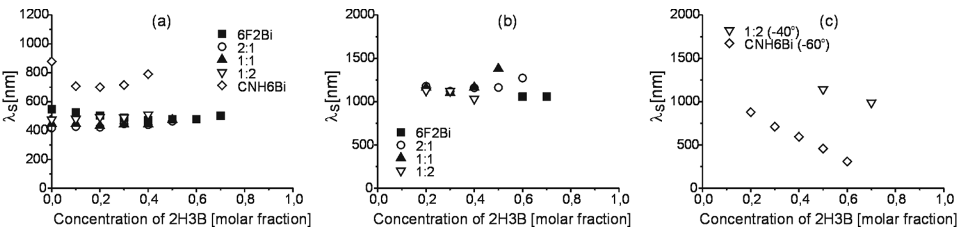


Figure 6. Wavelength of the selectively reflected light versus concentration of 2H3B for all tested systems in SmC* (a), high temperature SmC*$_A$ (b) and low temperature SmC*$_A$ (c).

ratio 2:1 mixed with 2H3B and then increase to value 800 nm for bicomponent mixture CNH6Bi-2H3B in SmC* phase, Figure 6a. In SmC*$_A$ phase all values of λ_s in higher temperature range ($T\text{-}T_{C^*A\text{-}C^*} = -10°C$) are in the region 1000 – 1500 nm, without simple relation with the concentration of CNH6Bi, Figure 6b. It can be observed at first the increase of values of λ_s and next the decrease with the increase of CNH6Bi. In SmC*$_A$ phase results of λ_s in lower temperature range ($T - T_{C^*A\text{-}C^*} = -40°C$ or $-60°C$) decrease with the increase of concentration of CNH6Bi, Figure 6c.

4. Conclusions

The analysis of results of mixing the low polar compound 2H3B with compounds of the higher polarity, responsible for the induction of SmC*$_A$ phase, having fluoroalkoxy group 6F2Bi or cyanogroup CNH6Bi, and their bicomponent mixtures in mole ratio 2:1, 1:1 and 1:2, shows that the compound 6F2Bi has more dominant role in the mixtures and more influences the induction of SmC*$_A$ phase in mixtures than CNH6Bi. The increase of the amount of CNH6Bi causes the decrease of the temperature and concentration range of existence of induced antiferroelectric phase. It also causes the shift of the concentration with the maximum temperature of SmC*$_A$ existence towards lower concentration of 2H3B. As found the temperature decrease of existence of the induced antiferroelectric phase is not linear with concentration of CNH6Bi.

The change of the helical pitch is different for the system with fluoroterminated compound than for the system with cyanoterminated compound in SMC_A^* phase. The pitch increases in the former case and decreases in the latter case with temperature. Also the helical twist sense is the opposite; the helix is right-handed in the former case and left-handed in the latter case. In three component mixtures the stepwise change is observed from characteristics of pitch typical for the bicomponent system with fluoroterminated component to characteristics typical for the bicomponent system with cyanoterminated component. Thus the increase of the concentration of cyanoterminated compound causes the increase of the pitch of right-handed helix and the decrease of the pitch of left-handed helix. The mixtures can be found with the helical twist sense inversion, similarly as it is observed for antiferroelectric phase formed by analogous pure compounds [10].

It should be mentioned that the decrease and next increase of the helical pitch values can be found both versus temperature as well as concentration in the tested systems.

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