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Small-angle X-ray scattering from binary liquid-crystalline mixtures of polar and non-polar compounds

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The phase diagrams of several binary mixtures consisting of cyanobiphenyls and different terminally non-polar mesogenic compounds exhibit induced smectic A phases. The smectic A layer spacing, d, of these induced phases have been investigated by small-angle X-ray scattering as a function of the molar fraction x_i. Large deviations of the layer spacings from the additivity rule $d_{\mathrm{mix}} = \Sigma\, x_i d_i$ have been observed in all mixed systems. Assuming a dimerization of the terminally polar compounds, the degree of association $\beta(x)$ was calculated as a function of composition for different dimerization constants. The theoretical relations $d_{\mathrm{mix}}(x)$ obtained from the calculated $\beta(x)$ values do not fit the experimental curves for $d(x)$. This fact can be interpreted by the formation of weak complexes between the polar and the terminally non-polar molecules of the binary mixtures. This kind of complexing seems to be responsible for the formation of induced smectic phases of the S_{Ad}-type and might disturb the monomer–dimer equilibrium $2M_p \rightleftharpoons D_p$ of the polar compounds.

1. Introduction

In binary mixtures of terminal strongly polar with terminally non-polar compounds induced smectic phases normally appear [1]. Often the smectic phase is most stabilized around a 1 : 1 molar ratio. De Jeu and Longa [2] have postulated that the majority of the induced smectic behaviour is connected with the formation of complexes. They distinguish between two situations.

(*a*) Strong complexing. The combination consists of a donor and an acceptor molecule. In these cases a charge transfer band is observed as direct evidence of an electron donor–acceptor complex.

(*b*) Weak complexing. Now the combination is an acceptor molecule and a neutral molecule in the sense that the electron donor properties of the latter, if any, are weak. This situation seems to apply to the majority of the mixtures with induced phases studied experimentally.

The aim of this paper is as follows. The X-ray investigations on three binary mixed systems, exhibiting induced smectic phases, should help in the understanding of the type of complexing on a molecular scale. We have measured therefore the smectic layer spacing, d, and the lateral intermolecular distance, s, as a function of composition. Additionally, the temperature dependence of d was investigated and, finally, the layer spacing of the mixed smectic phases has been calculated as a function of the composition, assuming a monomer–dimer equilibrium for the polar compound.

2. Experimental

The transition temperatures were measured with a polarization microscope (Leitz Ortholux 2-Pol BK). The X-ray measurements have been performed with a Kratky

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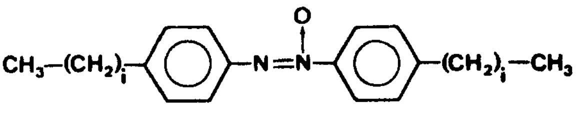
compact camera and a position-sensitive proportional counter, as described in detail in [3]. For film detection we employed a Kiessig camera and copper K_α radiation was used.

The formulae of the pure compounds used in the present study are

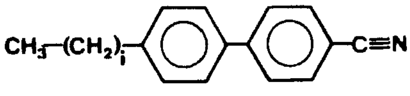
terminally non-polar:

C7 (i = 6), C10 (i = 9)

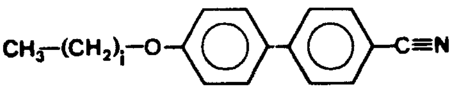


polar:

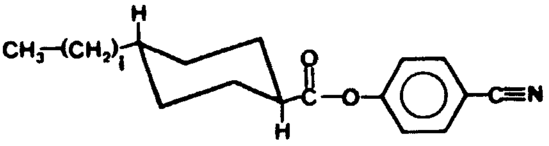
CB12 (i = 11)



11OCB (i = 10)



HPE (i = 3)



3. Experimental results

The phase diagrams of the binary mixtures investigated (see figures 1–3) exhibit induced smectic A phases with stabilization maxima shifted away from 50 mol % to higher concentrations of the terminally non-polar compounds. The smectic layer spacings versus molar fraction are shown in figures 4–6. They deviate greatly from linearity, which may occur in the limiting cases of either (*a*) no association (curves 1) or (*b*) total association of the polar compounds (curves 2). The increase of *d* with decreasing temperature is observed in all systems. As an example, the behaviour of the system CB12–C10 is shown in figure 7. The lateral intermolecular distance, *s*, depends on concentration with a maximum value of 0·54 nm, as shown in figure 8 for the system C10–HPE.

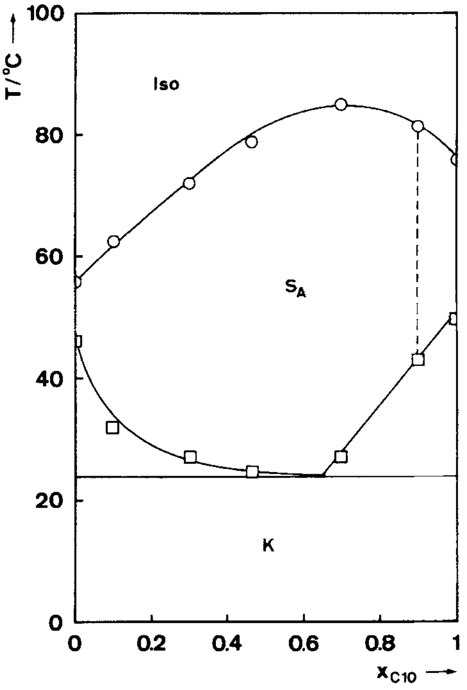


Figure 1. Phase diagram for the binary mixtures CB12–C10.

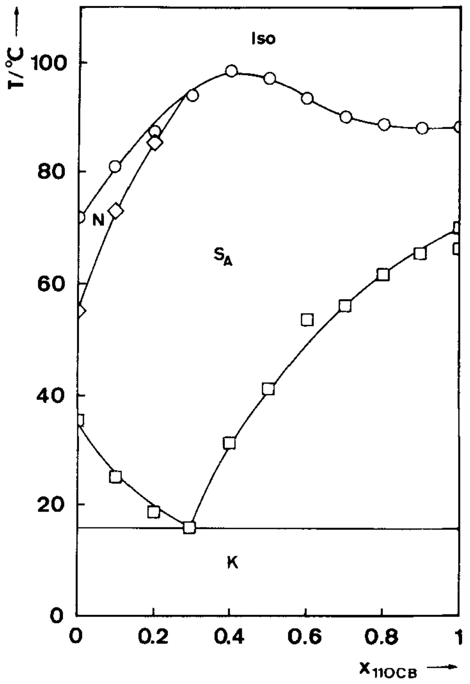


Figure 2. Phase diagram for the binary mixtures C7–11OCB.

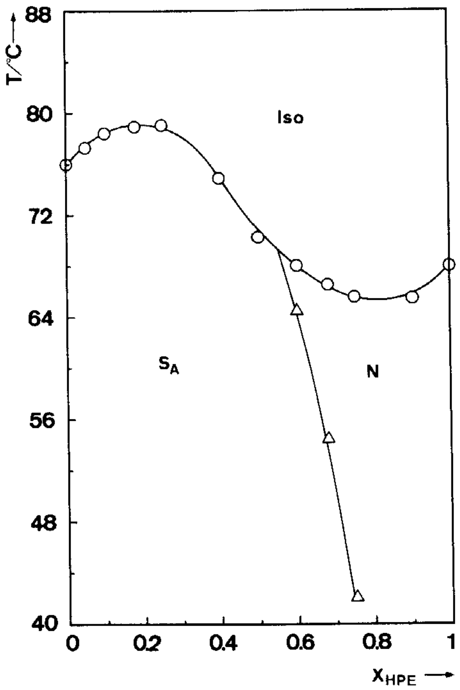


Figure 3. Phase diagram for the binary mixtures C10–HPE.

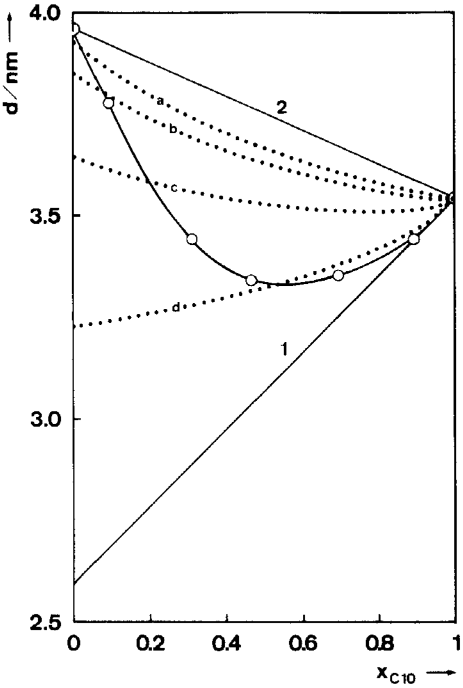


Figure 4. Smectic layer spacing, d_{exp} (○), of the system CB12–C10 versus molar fraction (curves 1 and 2; for a complete description see the text); (····) calculated d_{mix} values, parameter K_c in $cm^3 mol^{-1}$: (*a*) 10^6, (*b*) 10^5, (*c*) 10^4, (*d*) 10^3.

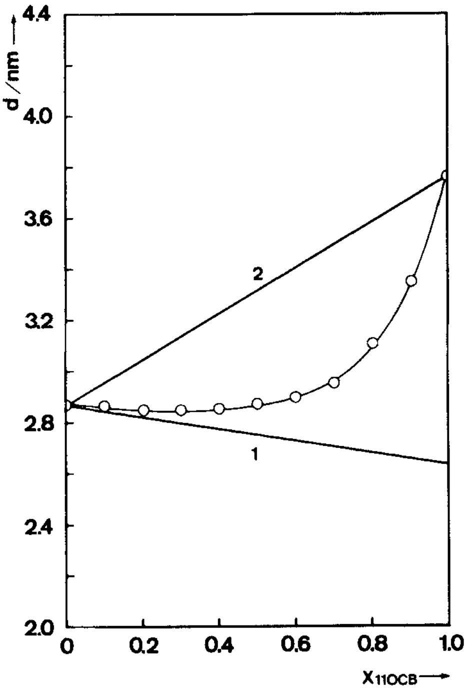


Figure 5. Smectic layer spacing d_{exp} of the system C7–11OCB versus molar fraction.

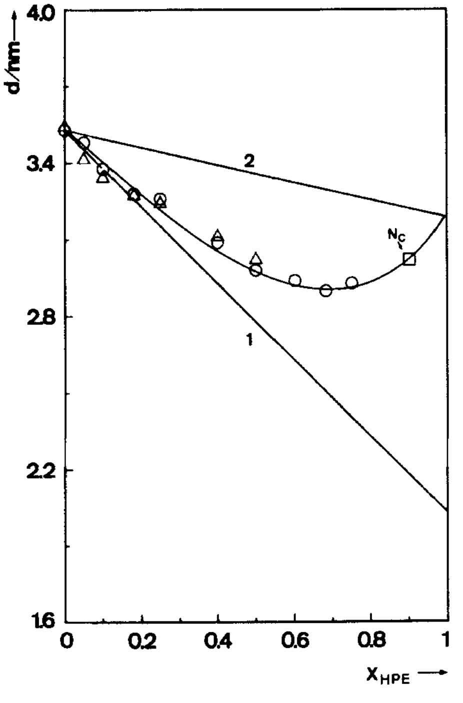


Figure 6. Smectic layer spacing, d_{exp}, versus molar fraction of the system C10–HPE. (○) PSPC, (△) film, (□) cybotactic nematic reflection.

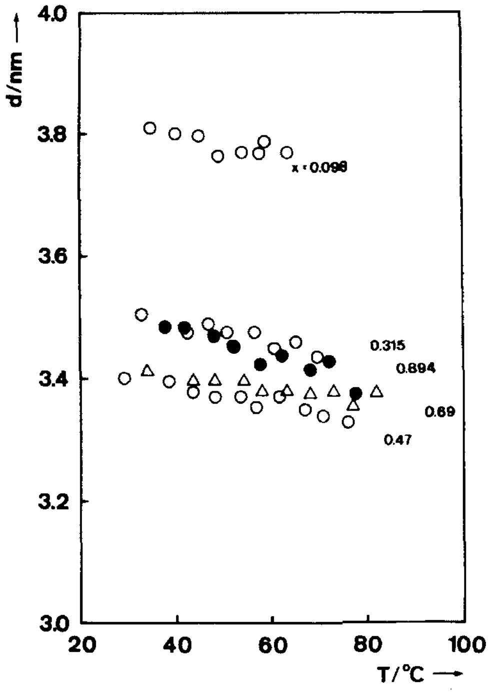


Figure 7. Temperature dependence of the layer spacing, *d*, for the system CB12–C10; parameter x_{C10}.

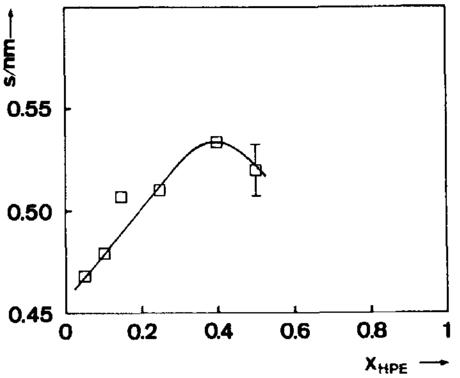


Figure 8. Lateral intermolecular distance, *s*, of the system C10–HPE versus molar fraction.

4. Numerical results

For binary mixtures of terminal polar with terminally non-polar compounds, there are in principle, two limiting situations.

(*a*) If the degree of association β of the polar compound is zero, then the layer spacing of the mixtures is given by

$$d_{mix} = d_u x_u + d_{pM} x_{pM}, \qquad (1)$$

where d_{mix} is the layer spacing of the mixture, d_u and d_{pM} denote the layer spacing of the pure terminally non-polar compound and the polar monomer, respectively, and x is corresponding molar fraction. The curves 1 in figures 4–6 reflect this behaviour.

(*b*) In the case of total association β equals unity and the layer spacing $d_{\mathrm{mix}}(x)$ is then given by

$$d_{\mathrm{mix}} = d_{\mathrm{u}}x_{\mathrm{u}} + d_{\mathrm{pD}}x_{\mathrm{pD}}, \tag{2}$$

where the index $\mathrm{p_D}$ refers to the polar dimer (cf. figures 4–6, curves 2).

Because of the large deviations of $d_{\mathrm{exp}}(x)$ from both of these additivity rules [4], calculations of d_{mix} as a function of the molar fraction of the polar compound (x_{p}) and the degree of association have been made with the following assumptions.

(*a*) The layer spacing d_{mix} is the arithmetic average of the layer spacings of all species, existing in the system

$$d_{\mathrm{mix}} = d_{\mathrm{u}}x_{\mathrm{u}} + d_{\mathrm{pM}}x_{\mathrm{pM}} + d_{\mathrm{pD}}x_{\mathrm{pD}}. \tag{3}$$

(*b*) The presence of a simple monomer–dimer equilibrium in the polar compound within the mixtures, which is not influenced by the terminally non-polar molecules

$$2M_{\mathrm{p}} \overset{K_{\mathrm{c}}}{\rightleftharpoons} D_{\mathrm{p}}. \tag{4}$$

(*c*) β equals unity for the pure polar compounds.

(*d*) Ideal mixing (e.g. no excess volume effects).

The relation between d_{mix} and x_{p} is then given by

$$d_{\mathrm{mix}} = [d_{\mathrm{u}} - x_{\mathrm{p}}(d_{\mathrm{u}} - d_{\mathrm{pM}}) + 0{\cdot}5\beta x_{\mathrm{p}}(d_{\mathrm{pD}} - d_{\mathrm{pM}})]/(1 - 0{\cdot}5\beta x_{\mathrm{p}}), \tag{5}$$

with

$$\beta = 1 - [(V_{\mathrm{m}}/4K_{\mathrm{c}}x_{\mathrm{p}})\,(1 + 8K_{\mathrm{c}}x_{\mathrm{p}}/V_{\mathrm{m}})^{0{\cdot}5} - 1)]; \tag{6}$$

this equation is derived in [5]. The theoretical values d_{mix} (see figure 4), β (see figure 9) and c_{i} (see figure 10) have been calculated for different values of the association constant K_{c} and are shown, as an example, for the system CB12–C10. The molar volumes of the pure compounds have been taken from the literature [6, 7].

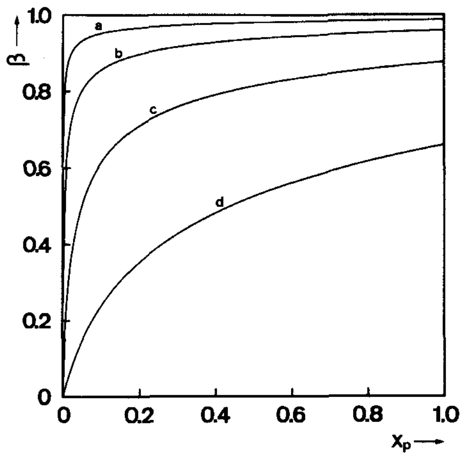


Figure 9. Degree of association β as a function of molar fraction x_{CB12} of the system CB12–C10; parameter K_{c} (cf. figure 4).

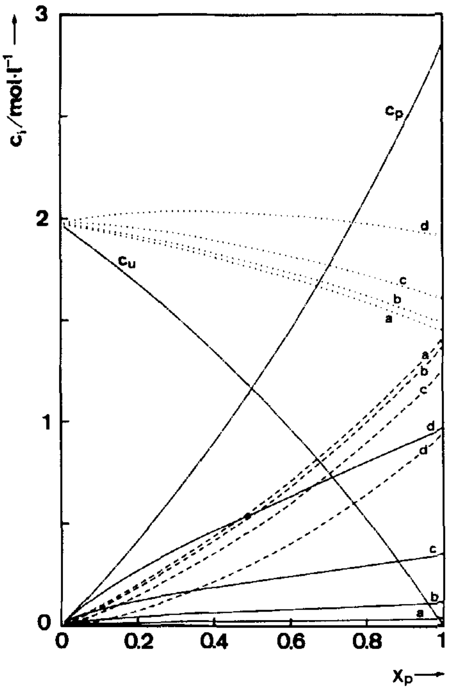


Figure 10. Concentrations of all species in the system CB12–C10 versus molar fraction x_{CB12}; (· · ·) $c_s = c_u + c_{pM} + c_{pD}$, (——) c_{pM} (—·—) c_{pD}, $c_p = c_{pM} + 2c_{pD}$. Parameter K_c (cf. figure 4).

5. Discussion

The shift of the stabilization maximum of the present induced smectic phases, shown in the phase diagrams, to higher concentrations of the terminally non-polar compounds is attributed to a higher tendency to form smectic phases in non-polar compounds. We refer to this tendency as the smectogenicity of a molecule. In general, the conclusion is that the smectogenicity of molecules forming an ordering smectic A phase is higher than of those forming an S_{Ad} phase. An instructive example for this behaviour has been given by Sigaud *et al.* [8]. In mixtures of the mesogenic cyanobicyclohexane derivative CCH4 with a non-mesogenic polyaromatic compound, they found an induced smectic phase with a maximum stability at high concentrations of the mesogenic compound ($x_{\mathrm{meso}} = 0{\cdot}82$). Obviously, the smectogenicity of mesogenic molecules is higher than of non-mesogenic compounds and, in principle, the shift of the stabilization maximum of induced smectic phases can be understood in terms of smectogenicity.

Because of the different layer spacings, we can differentiate between the types of smectic A phases. In the systems investigated two types have been observed. The pure terminally non-polar compounds exhibit ordinary S_A phases of the monolayer type, where the ratio of the layer spacing to the molecular length (alkyl chains in their all-*trans* configuration) is about 0·9. The pure polar compounds form S_{Ad} phases, whose aggregates are dimers, characterized by the ratio $d/L \approx 1{\cdot}5$. The S_A phase shown in the phase diagrams is not uniform for these experimental results and a phase transition S_A–S_{Ad} should take place with increasing molar fraction. Under the microscope this phase transition has not been observed and by differential scanning calorimetry no evidence for a first order transition could be found. Because of this, the phase transition must become second order with increasing molar fraction.

The vertical broken line in figure 1 roughly marks the boundary between the S_A and the S_{Ad} phase. The conclusion from the results of the layer spacings in the system CB12–C10 is that at molar fractions $x_{C10} \geqslant 0{\cdot}9$ only monomers exist (cf. figure 4). Therefore, at high concentrations of the terminally non-polar compound an S_A phase is present.

The continuous change of symmetry, which is connected with the second order transition, requires a monomer–dimer equilibrium in the polar compound. Additional evidence for the presence of such an equilibrium in the mixtures are given by the following experimental results.

(*a*) The slight increase of the layer spacing with decreasing temperature (see figure 7) may be attributed to the formation of dimers, which is straightforward because of the temperature dependence of the association constant given by

$$K_c = \exp(\Delta E/RT), \tag{7}$$

with $\Delta E = E_{\text{dimer}} - 2E_{\text{monomer}} < 0$.

The energy of a dimer is significantly less than that of two monomers, so equation (7) leads to higher values of K_c with decreasing temperature and, consequently, from equation (4) the shifting of the equilibrium to the dimers follows.

(*b*) The lateral intermolecular distance, s, for the pure terminally non-polar compound is about 0·47 nm, which is a standard value for non-polar smectics. A strong increase of s with the molar fraction of the polar compound can be understood with some form of dimerization. The average value of s reaches 0·54 nm for $x_{\text{HPE}} = 0{\cdot}4$. The decrease of s with higher concentrations of HPE cannot be understood yet.

(*c*) The large deviations of the layer spacing as a function of the molar fraction from the situations with constant β values (cf. equations (1) and (2)) have to be associated with a variation of β with concentration.

For the lowest value of K_c (1000 $\text{cm}^3\,\text{mol}^{-1}$) the calculated $d_{\text{mix}}(x)$ values (see figure 4, curve *d*) fit very well with the experimental *d* values at high concentrations of C10 ($x_{C10} > 0{\cdot}6$). At high concentrations of the polar compound the theoretical curve cannot reach the experimental *d* values. In contrast, for the highest chosen value of K_c ($10^6\,\text{cm}^3\,\text{mol}^{-1}$), which is a standard value for dissolved carboxylic acids [9], the theoretical and calculated *d* values coincide for high concentrations of CB12, but not for high values of x_{C10} (cf. figure 4, curve *a*).

For the K_c values chosen between these two extremes the theoretical *d* values never fit the experimental curve. For this reason it is obvious that it would not be successful to work with an average value of K_c instead of a concentration dependent association constant to describe a monomer–dimer equilibrium with molar fraction in a mixed system.

It seems that the assumption of a simple monomer–dimer equilibrium of the polar compound is not justified. However, in contradiction to our assumption of a simple monomer–dimer equilibrium (cf. equation (4)), the equilibrium is influenced by the terminally non-polar compound. Only a concentration dependent association constant is able to explain the experimental fact of small β values at low concentrations of the polar compound and very high β values at a high molar fraction x_p.

In conclusion, our results indicate that the formation of weak but specific complexes between terminally non-polar molecules on the one hand and polar monomers or dimers on the other hand is the competing process to the dimerization. However, this complexing is the driving process for the formation of induced smectic phases in the mixed systems under discussion.

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