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Influence of structure on smectic A–smectic A phase separation

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The critical temperature at the consolute point where two smectic A phases of different compositions phase separate has been measured for binary systems which combine one compound from a newly synthesized series of fluorinated mesogens with one homologue from the commercially available cyanobiphenyl family. Taking advantage of the regular evolution of the layer spacings within a series of homologues, this systematic analysis identifies a clear connection between miscibility and difference in layer spacings of the smectic A phases of the pure compounds. However, additional data obtained on significantly different systems show the non-universal character of this analysis and suggest that factors in addition to this structural difference are relevant to this phenomenon.

1. Introduction

A few years ago we described the first example of a consolute point in a smectic A solution of two thermotropic liquid crystals [1, 2]. This result was obtained with binary mixtures of a highly fluorinated mesogen and a polar cyano-mesogen. This peculiar combination of compounds obviously suggests two causes for this phase separation: (i) the antipathic interaction among fluorocarbon and hydrocarbon chains and (ii) the difference in layer spacing between the smectic structures of the pure compounds (monomolecular layers of the fluorinated compound opposed to partial bilayers of the cyano compound). We have already briefly discussed these points in a recent study of smectic A solutions of a liquid crystalline polymer dissolved in a molecular mesogen. This work supported, from a qualitative point of view, the influence of the layer structure and layer thickness on the phase separation in systems involving fluorinated and non-fluorinated compounds as well. Of course the difference in overall molecular size of the components was also important in driving phase separation in these macromolecular solutions [3].

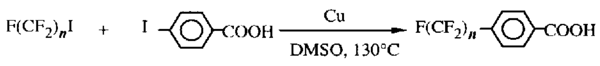
In the present paper we extend our investigations to solutions of two molecular mesogens in the smectic A phase. Each of the binary systems involves a molecule with a perfluorinated end chain of variable length from a new thiobenzoate homologous series, and a classical cyanobiphenyl with a fully perhydrogenated end chain of variable length. A comprehensive ensemble of coordinates of consolute points is obtained from this family of phase diagrams. Considering that changing either the fluorine content through the number of perfluorinated segments in the first type of molecule or the number of methylene segments in the aliphatic chain of the polar compounds modifies simultaneously their layer spacings in the smectic A phase, a matrix comparison of the data allows discussion of the respective roles of the antipathic molecular interaction and of the mismatching of layer spacings.

2. Materials

The perfluorinated mesogens used in the present studies are based on a thiobenzoate core [4]. These materials are obtained by esterification of a 4-perfluoroalkylbenzoic acid with a 4-alkoxythiophenol:

The acid and phenol moieties are not commercially available and need to be synthesized as follows:

(i) synthesis of the 4-perfluoroalkylbenzoic acids



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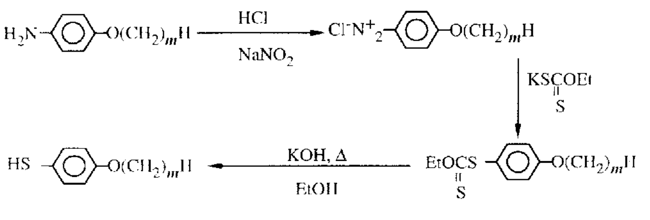
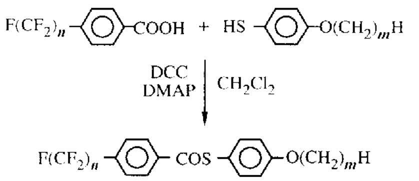
(ii) synthesis of the 4-alkoxythiophenols

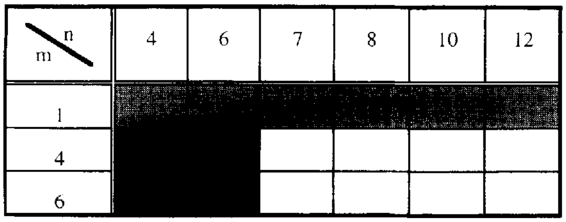


esterification leads to the final product



The filled rectangles in figure 1 summarize the combinations of chain lengths which have been obtained. All compounds are mesomorphic and their phase behaviour has been characterized through polarized optical microscopy and differential scanning calorimetry. These properties, together with full structural data, will be described in a later paper. For this miscibility study, we provide in table 1 the transition temperatures for the four compounds used (dark grey rectangles in figure 1).

One can first remark that all these mesogens possess a single liquid crystalline state of the smectic A type which is usual for molecules combining at each end a perfluorinated tail and a perhydrogenated chain [4]. The second point of interest concerns the values of the melting and clearing temperatures: the former are remarkably low owing to the thiobenzoate bridging group in the central part of the molecule and the latter are significantly increased compared to the commonly studied benzoate homologues (for example the thiobenzoate with $n = 8$, $m = 1$ melts at 115·7°C and clears at 162·3°C, while these phase changes occur, respectively, at 128·4°C and 134·6°C for the benzoate analogue). This characteristic is essential in order to provide a mesomorphic range that is as large as possible to have a chance of driving phase separation by lowering the temperature.



m \ n	4	6	7	8	10	12
1	▨	▨	▨	▨	▨	▨
4	■	■				
6	■	■				

Figure 1. Summary of compounds synthesized (grey rectangles) in the series $F(CF_2)_nPhCOSPhO(CH_2)_mH$. Dark grey indicates the 4 compounds actually used in the miscibility studies.

Table 1. Transition temperatures in °C for the compounds $F(CF_2)_nPhCOSPhO(CH_2)_mH$ specifically used in the present miscibility studies.

n	m	Cr		S_A		I
4	4	•	47	•	114	•
4	6	•	50	•	107	•
6	4	•	67	•	144	•
6	6	•	59	•	131	•

Each of the previous fluorinated compounds has been combined with the well known 4-alkoxy- and 4-alkyl-4′-cyanobiphenyls (*n*OCB and *n*CB from Merck Ltd.) with n ranging in each case between 9 and 12, for which the liquid crystalline properties are recalled in table 2. Comparison of tables 1 and 2 shows the satisfactory matching of the liquid crystalline ranges among the compounds of the two families, which is also a required condition for miscibility studies. Optical microscopy has been mainly used to investigate the thermal stability of these smectic A solutions.

3. Experimental

Initially the contact method [5] was used to select which among the above systems offer a gap in miscibility and, further, to detect the critical temperature at the consolute point when observed. Applying this technique requires preferably a homeotropic alignment within the contact zone which makes it easier to detect the occurrence of a phase separation line cutting its way into a homogeneous grey background (figure 2) (uncrossing the polarizer and the analyzer to a greater or lesser degree is often useful, because of the faintness of the phenomenon). In those cases where crystallization of the pure cyanobiphenyl would have prevented achievement of a sufficiently low temperature to obtain the phase separation line, we have used instead a mixture low in

Table 2. Transition temperatures in °C for the *n*OCB $[H(CH_2)_nOPhPhCN]$ (upper part) and *n*CB $[H(CH_2)_nPhPhCN]$ (lower part) used as second components in the binary systems.

Compound type	n	Cr		S_A		N		I
*n*OCB	9	•	64	•	77	•	80	•
	10	•	59	•	84	—		•
	11	•	71	•	87			•
	12	•	70	•	90	—		•
*n*CB	9	•	42	•	48	•	50	•
	10	•	44	•	51	—		•
	11	•	53	•	58			•
	12	•	48	•	59	—		•

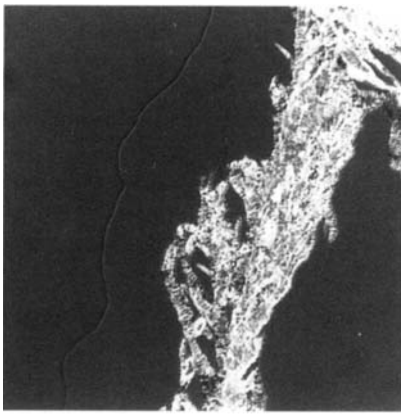


Figure 2. Characteristic phase line for phase separation between two S_A phases as observed by polarizing microscopy (slightly uncrossed polarizer and analyzer).

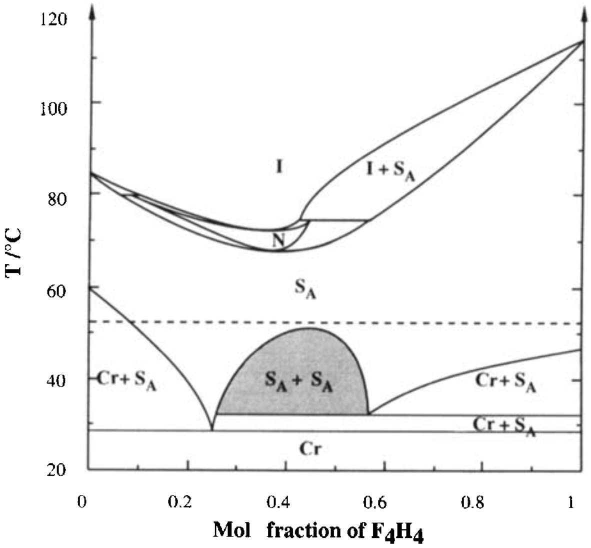


Figure 3. Phase diagram of the binary system F_4H_4–10OCB. The dashed line corresponds to the isotherm line at which the layer spacings in the homogeneous smectic A state have been measured as a function of composition (see figure 5).

concentration of fluorinated compound and rich in cyanobiphenyl in contact with the pure fluorinated compound. All pair combinations involving the four fluorinated compounds in table 1 and the eight cyanobiphenyls in table 2 have been tested this way. The critical temperatures are reported in tables 3(*a*) and 3(*b*). For a better understanding, an example of a complete phase diagram (F_4H_4–10OCB), based on observations made on mixtures at defined compositions, which can be regarded as typical for all the systems is presented in figure 3.

The layer spacings in the smectic A phase have been systematically measured for all compounds, including the cyanobiphenyls, as powder samples using a photographic Guinier chamber and a Co $K_{\alpha 1}$ monochromatic beam. The resolution is estimated to 0·1 Å. These data are presented in table 4. The values of the ratio d/L (layer spacing over molecular length) are also given in

Table 3(*a*). Temperatures at the consolute point as measured by the contact method on systems involving the **4-alkoxy**-4′-cyanobiphenyls. (N.A.: no consolute point observed prior to crystallization of the sample). $\Delta T = T_{c\,exp\,SA} - T_{c\,calc\,iso}$; for Δd see text.

Binary systems						
n (C_nF_{2n+1})	m (C_mH_{2m+1})	nOCB	$T_{c\,exp\,SA}$ /K	$T_{c\,calc\,iso}$ /K	ΔT /K	Δd /Å
4	4	12	340·8	55·8	285	13·3
4	4	11	335·9	67·1	269	11·3
4	4	10	332·6	80·4	253	9·5
4	4	9	314·0	95·1	219	7·9
6	4	12	370·2	115·2	255	10·4
6	4	11	344	131·2	213	8·4
6	4	10	337	149·9	187	6·6
6	4	9	324·1	169·1	155	5
4	6	12	327·4	72·4	255	12
4	6	11	298·3	86·3	212	10
4	6	10	284	102	182	8·2
4	6	9	273·4	118·4	155	6·6
6	6	12	335·5	136·3	200	9
6	6	11	322·9	153·4	170	7
6	6	10	311·8	172·6	139	5·2
6	6	9	N.A.	193·4	—	3·6

Table 3(*b*). Temperatures at the consolute point as measured by the contact method on systems involving the **4-alkyl**-4′-cyanobiphenyls. (N.A.: no consolute point observed prior to crystallization of the sample). $\Delta T = T_{c\,exp\,SA} - T_{c\,calc\,iso}$; for Δd see text.

Binary systems						
n (C_nF_{2n+1})	m (C_mH_{2m+1})	nCB	$T_{c\,exp\,SA}$ /K	$T_{c\,calc\,iso}$ /K	ΔT /K	Δd /Å
4	4	12	N.A.	41·9	—	14·2
4	4	11	312·3	53·5	258·8	12·6
4	4	10	299·7	66·1	233·6	10·4
4	4	9	289·7	79·4	210·3	8·7
6	4	12	N.A.	91·2	—	11·3
6	4	11	N.A.	107·7	—	9·7
6	4	10	313·5	124·9	188·6	7·5
6	4	9	301	142·7	158·3	5·8
4	6	12	300·2	57·4	242·8	12·9
4	6	11	N.A.	70·9	—	11·3
4	6	10	N.A.	85·3	—	9·1
4	6	9	N.A.	100·5	—	7·4
6	6	12	316·2	114·8	201·4	9·9
6	6	12	308·2	133·4	174·8	8·3
6	6	10	N.A.	152·5	—	6·1
6	6	9	N.A.	171·9	—	4·4

Tables 4(*a*) (top), 4(*b*) (middle), 4(*c*) (bottom). *d* (layer spacing, experimental) and *L* (molecular length from stereomodels) in Å, ΔE_{vap} in cal mol^{-1}, *v* in cm^3 mol^{-1}, δ in cal$^{1/2}$ cm$^{-3/2}$ (all calculated, see text).

m (C_mH_{2m+1})	*n* (C_nF_{2n+1})	*d*	*L*	*d*/*L*	ΔE_{vap}	*v*	δ
4	4	25·3	25·2	1·01	32455	337	9·8
6	4	26·6	27·0	0·98	34815	370	9·7
4	6	28·2	28·0	1·01	34495	383	9·5
6	6	29·6	30·5	0·98	36855	416	9·4

*n*OCB	*d*	*L*	*d*/*L*	ΔE_{vap}	*v*	δ
9	33·2	25·8	1·28	36075	304	10·9
10	34·8	27·1	1·28	37255	320	10·8
11	36·6	28·3	1·29	38435	336	10·7
12	38·6	29·3	1·31	39615	352	10·6

*n*CB	*d*	*L*	*d*/*L*	ΔE_{vap}	*v*	δ
9	34	24·3	1·40	35275	300	10·8
10	35·7	25·4	1·40	36455	316	10·7
11	37·9	26·8	1·41	37635	332	10·6
12	39·5	28·4	1·40	38815	348	10·5

this table; they show that our fluorinated compounds can be classified as smectic A with monomolecular layers ($d/L \approx 1$, S_{A1} or S_{Am} according to the nomenclature in use) and they remind us that the smectic A phases of cyanobiphenyls belong to the partially bimolecular smectics identified as S_{Ad} ($1 < d/L < 2$). Note that an S_{A1} structure with $d/L \approx 1$ for the fluorinated compounds indicates that the molecules are not tilted and suggests that no microphase separation exists among fluorinated, aromatic and aliphatic parts within the layers.

4. Discussion

The critical temperature, T_c, is the key parameter which is sensitive to any modification of the interactions in binary solutions. The regular increase of T_c as a function of cyanobiphenyl chain length within a given series of measurements is conspicuous in table 3. Qualitatively, this looks consistent with classical measurements made on mixtures of *n*-alkanes and *n*-perfluoroalkanes [6, 7], although only a very few binary systems involving the shortest homologues (CF_4, C_2F_6) could serve for comparison. The same comment applies to the increase of T_c with the length of the perfluorinated chain at constant hydrogenated chain length and constant cyanobiphenyl. No comparison can be made regarding the decrease of T_c with the length of the hydrogenated chain at constant perfluorinated chain and constant cyanobiphenyl.

However, strong deviations of the experimental results from the otherwise satisfactory Flory–Huggins (F–H) model was clearly stressed in the classical studies of these mixtures of linear fluorinated and hydrogenated chains; no satisfactory explanation can still be given to these exceptions. Thus, to achieve comparison of our data with the F–H model we have calculated the critical temperatures using equations (1) and (2) in order to check whether such differences appear in our systems.

$$\delta_i = \left(\frac{\Delta E_{\mathrm{vap.i}}}{v_i}\right)^{1/2} \tag{1}$$

$$T_{\mathrm{c\,calc\,iso}} = \frac{2}{R}(\delta_2 - \delta_1)^2 \frac{v_1 v_2}{(v_1^{1/2} + v_2^{1/2})^2} \tag{2}$$

The evaluations of molar volumes (v_i), energies of vaporization ($\Delta E_{\mathrm{vap,i}}$), solubility parameters (δ_i) and of the interaction parameter [8] of our compounds have been conducted using the method of increments proposed by Fedors [9], see tables 4(*a*), 4(*b*) and 4(*c*). We stress that the temperatures, $T_{\mathrm{c\,calc\,iso}}$, derived from this semi-empirical method represent the expected position of the consolute point *if the phase separation were to occur in the isotropic state of a regular solution.* The $T_{\mathrm{c\,calc\,iso}}$ values are listed in tables 3(*a*) and 3(*b*) next to the experimental $T_{\mathrm{c\,exp\,SA}}$ values for which the subscript recalls that they are all measured within the smectic A domain. Large positive differences are obvious between $T_{\mathrm{c\,exp\,SA}}$ and $T_{\mathrm{c\,calc\,iso}}$. To analyze our data we decided to consider the difference $\Delta T = T_{\mathrm{c\,exp\,SA}} - T_{\mathrm{c\,calc\,iso}}$ which can be considered as representative of the influence of the anisotropic environment on the interaction parameter.

On the other hand, the free energy describing such mixtures of smectics involves a coupling term between composition and layer spacings as shown in the following expression taken from Nallet *et al.* [10] written in terms of the layer displacement *u* and the deviation *c* from the mean mesogen concentration:

$$f = \frac{1}{2}B(\partial_z u)^2 + \frac{1}{2}K(\nabla_\perp^2 u)^2 + \frac{1}{2}\chi^{-1}c^2 + C_c c\,\partial_z u$$

in which *f* is the free energy density, *B* the smectic compressional modulus at constant concentration and *K* the bending elasticity. The coupling term $C_c c\,\partial_z u$ expresses the fact that the layer spacing depends on composition. If pure phases have a relative difference $\Delta l/l_0$ in layer spacing, we should expect $C_c \approx B\Delta l/l_0$ [10].

These arguments lead to a plot of the ΔT values as a function of the differences in layer spacings between the smectic A structures of the two pure compounds participating in the mixture, $\Delta d = d_{n\mathrm{OCB}} - d_{\mathrm{F}n\mathrm{H}m}$ (see figure 4(*a*) for systems involving the alkoxycyanobiphenyls and

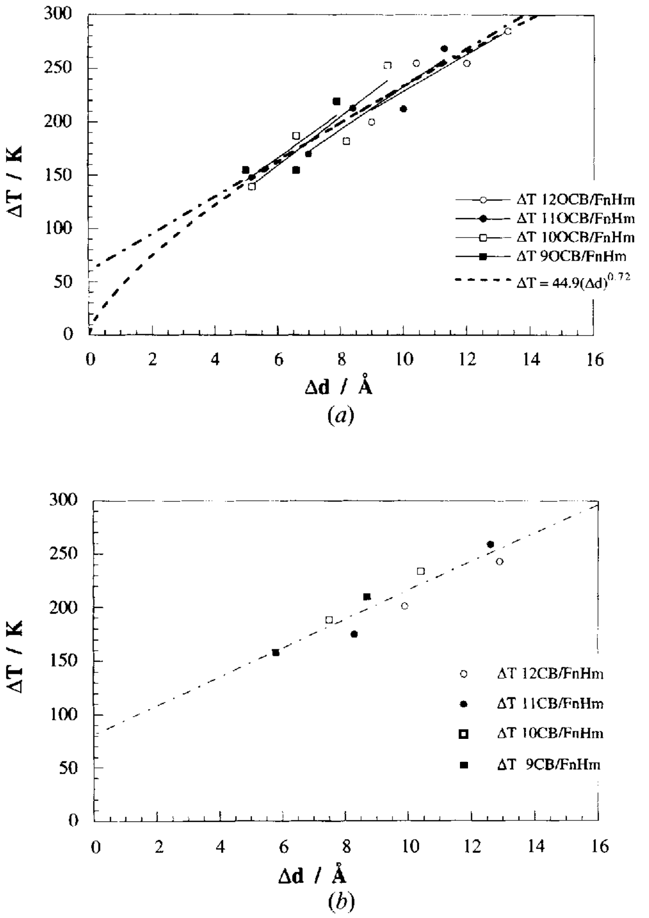


Figure 4(*a*). Evolution of the excess contribution (with reference to the model of regular solutions) to the critical temperatures as a function of the difference in layer spacings Δd for nOCB–F_nH_m pairs (see text for a discussion of the different kinds of fits). (*b*). Evolution of the excess contribution (with reference to the model of regular solutions) to the critical temperatures as a function of the difference in layer spacings Δd for nCB–F_nH_m pairs.

figure 4(*b*) for systems involving the alkylcyanobiphenyls). The various symbols in both figures indicate the evolution of ΔT 'for a constant cyanobiphenyl solvent' on varying the 'fluorinated solutes'.

The solid lines in figure 4(*a*) are individual linear fits for the four sets of data. They clearly show a good correlation between the anomalous ('anistropic') part of the critical temperature and the difference in layer spacing of the components. Moreover, they all lie very close to the best linear fit including all data points (the dashed and dotted line) which indicates a satisfactory consistency among the data. Thus, a linear function seems to account for the influence of the difference in layer spacings over the range of Δd values which could be investigated with our systems. Despite fewer points, the alkyl data in figure 4(*b*) confirm this seemingly linear behaviour.

Interestingly, the intercepts of the linear fits with the ΔT axis show clearly a residual value when the difference in layer spacings vanishes, as if the anomalous part of the interaction parameter has some other cause than a difference in layer spacings. This observation could be interpreted either by coupling with the orientational order parameter and/or by specific in-layer interaction between oriented perfluoroalkyl and hydrocarbon parts which, as noted previously for isotropic fluorocarbon–hydrocarbon solutions, would result by itself in significant deviations from the regular solution calculations. Of course, another possibility is a large systematic uncertainty in the $T_{\mathrm{c\,calc\,iso}}$ values resulting from the method of molecular increments. Finally, one can argue that the variation of ΔT could not be proportional to Δd all the way through zero. As an example we have chosen arbitrarily a power law fitting including the origin (dashed curve in figure 4(*a*)) which looks as good as the linear one within the range of experimental data.

In these systems one can note that the large difference in layer spacings is obtained owing to the monomolecular layer structure of the perfluorinated compounds (labelled $S_{A1\ \mathrm{or}\ m}$) opposed to the well known partially bilayer smectic A structure of the cyanobiphenyls (labelled S_{Ad}) which results from their polar molecular structure (the first system described in [1] combined similarly a polar cyano compound and a fluorinated benzoate). At this point one is faced with the two following questions: (i) does the consolute point coincide with a change from S_{Ad} to S_{A1}?; (ii) are the structural and molecular peculiarities of cyano compounds essential to the observed S_A–S_A phase separation?

The measurement of the layer spacings as a function of composition along an isotherm located just above the critical temperature in the homogeneous smectic A phase

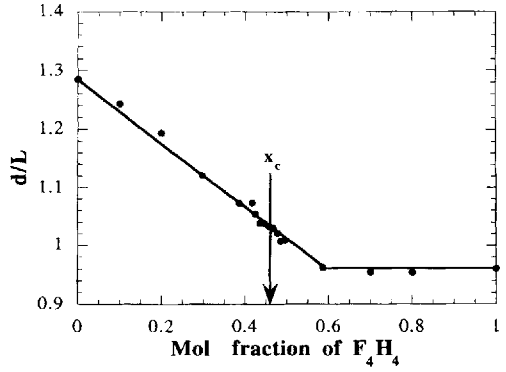


Figure 5. Evolution of the d/L ratio as a function of composition for the F_4H_4–10OCB binary system. $T > T_c$ by one degree.

Table 5. Characteristics of the mesogens **A** and **B** used for S_{A1}–A_{A1} phase separation. T in °C; d, L in Å; ΔE_{vap} in cal mol^{-1}; v in cm^3 mol^{-1}; δ in cal$^{1/2}$ cm$^{-3/2}$.

	Polymorphism							Exp		Calculated		
Compound	Cr		S_C		S_A		I	d	L	ΔE_{vap}	v	δ
A	•	91	•	102	•	122	•	32·5	35·5	42700	520	9·1
B	•			47	•	145	•	23·2	23·2	32190	277	10·8

Table 6. Comparison of the experimental and calculated (from F–H theory) critical volume compositions for nOCB–F_nH_m pairs. φ_c is the volume fraction of fluorinated compound.

Volume fraction	System					
	F_4H_4–10OCB	F_4H_4–11OCB	F_4H_4–12OCB	F_6H_6–10OCB	F_6H_6–11OCB	F_6H_6–12OCB
$\varphi_{c\,exp\,SA}$	0·48	0·50	0·51	0·37	0·43	0·44
$\varphi_{c\,calc\,iso}$	0·49	0·51	0·53	0·41	0·43	0·45

of the F_4H_4–10OCB binary system (see figure 3) provides some elements in answer to the first question. Figure 5 shows that there actually exists a sharp change in the smectic structure at $x_{F_4H_4} = 0{\cdot}58$. However the position of the critical composition, $x_c = 0{\cdot}46$ (fluorinated fraction), looks sufficiently different to conclude that there is no clear connection between the two phenomena. The separation (in this system) appears then to involve two weakly partially bimolecular smectics and could be classified as S_{Ad}–S_{Ad} type (the theory of frustrated smectics suggests such a type of critical point in polar systems). Moreover one can check in figure 6 that the layer spacings of pure compounds are dependent on temperature. This remark applies to all mixtures.

In parallel with the systematic study of the cyanobiphenyl solutions described above, we have expanded our investigations to many other associations of fluorinated and non-fluorinated compounds including non-polar compounds. These new studies have provided an answer to the second question, since we have discovered at least one example of a consolute point involving two monomolecular smectics (S_{A1}–S_{A1} type). This system is highly important, for it gives evidence that neither a cyano polar compound nor a partially bilayer structure is required for phase separation. The characteristics of this (so far unique) pair are described below and in table 5:

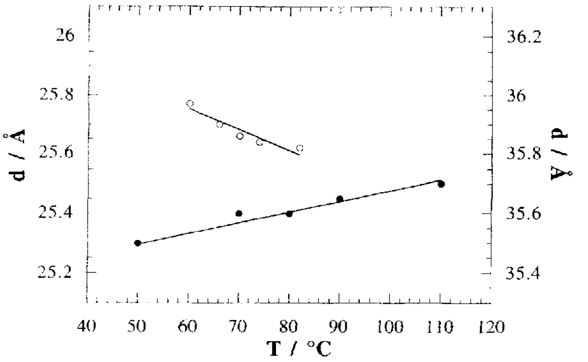
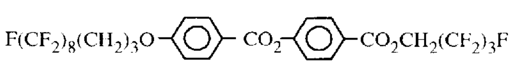


Figure 6. Layer spacing as a function of temperature for the two pure compounds: F_4H_4 (filled circles) left axis, 10OCB (open circles) right axis.

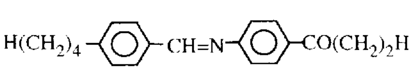
The topology of the **A–B** phase diagram is not basically different from the topology sketched in figure 3 for the previous systems. However there is no nematic phase observed and the location of the consolute point is, in this case, strongly shifted towards the compositions richer in non-fluorinated compound ($x_{Ac} \approx 0{\cdot}14$).

As for the critical temperature characterizing the **A–B** system, we have measured $T_{c\,exp\,SA} = 388$ K to be compared to $T_{c\,calc\,iso} = 280$ K. In this case too there exists a large positive difference, $\Delta T = 108$ K, between the experimental and calculated values. However, if one locates the point $\Delta d = 9{\cdot}3$ Å, $\Delta T = 108$ K, representing the **A–B** system in figures 4 (*a*) or 4 (*b*), it appears clearly out of the area where the data for the previous series with cyanobiphenyls are found. Thus it seems that no 'universal behaviour' can be attached to the good consistency noted for the results obtained with homologous compounds of the alkoxy- and alkyl-cyanobiphenyl family.

Note also that in this case of S_{A1}–S_{A1} phase separation,



(A)



(B)

the difference in molecular lengths and consequently in layer spacings is such that the layers of the fluorinated compound are larger than those of the non-fluorinated one. Varying the molecular length in the families of compounds **A** and **B**, as we did with the cyanobiphenyls, has not been productive because of the reduced smectic A range of the fluorinated mesogen **A**. Nevertheless, it can be qualitatively observed that decreasing the length of compound **B** by one methylene group on the left side (i.e. increasing the difference in layer spacings) results in an increase of the temperature of phase separation. But the increase is such that the phase separation now occurs at a triple point of eutectoid topology where the isotropic liquid transforms directly into two smectic A phases of different composition upon cooling ; this means that a 'virtual consolute point', if any, would exist at some higher temperature, in any case above 388 K. At the opposite side, increasing similarly the length of compound **B** results undoubtedly in a decrease of the temperature of phase separation, but in this case no S_A–S_A phase separation could be reached prior to the occurrence of a smectic C phase and ultimately crystallization.

The analysis of the critical compositions is costly in materials compared to the measurement of the critical temperatures. Yet we have determined this parameter for a selection of systems. Small quantities (c. 20 mg) of various mixtures of given compositions (separated by 5% steps) were prepared and observed for phase separation by polarizing microscopy. A rough boundary of the miscibility gap could then be drawn from which the values of $\varphi_{c\,\exp\,SA}$[†] were evaluated with an uncertainty of about ±2%.

$$\left(\frac{\varphi_2}{\varphi_1}\right)_c = \left(\frac{v_1}{v_2}\right)^{1/2} \qquad (3)$$

These are reported in table 6 and compared with $\varphi_{c\,\mathrm{calc\,iso}}$ values calculated from equation (3) given by the F–H model for regular solutions. The rather good agreement suggests that the critical composition in nOCB–F_nH_m pairs is not greatly dependent on the smectic environment, since the expression above is valid in the isotropic state. For the **A–B** system we have determined $\varphi_{c\,\exp\,SA} = 0{\cdot}24$ and evaluated $\varphi_{c\,\mathrm{calc\,iso}} = 0{\cdot}42$. This result for the S_{A1}–S_{A1} phase separation also appears out of range with respect to the behaviour of nOCB–F_nH_m mixtures. In this case, one is led to propose an arrangement of the two kinds of molecule to form a monomolecular layer to interpret the shift of the critical composition. In the case of nOCB–F_nH_m systems, both compounds have roughly the same molecular length, although the layer spacings can be much different owing to the dipolar pairing of the nOCB component. From a simple steric point of view, one nOCB molecule will not introduce a large local modification of a layer rich in F_nH_m, and at the opposite side, it is only a matter of breaking some loose dimers within a layer rich in nOCB to match the perturbation in layer thickness created by one F_nH_m molecule. The situation is less relaxed in the **A–B** system because the difference in layer spacings is intrinsically connected to the molecular lengths. A layer made of short **B** is likely to accept with difficulty such a large molecule as **A**[‡]. At the opposite side, it is certainly less costly for a layer made largely of **A** to accommodate a molecule of **B** making the phase diagram unsymmetrical. This would explain why the behaviours of nOCB–F_nH_m and **A–B** systems are so different with regard to the critical composition and temperature.

5. Conclusion

The systematic part of this study conducted with two groups of parent compounds gives evidence for the prominent role of the layer spacings in phase separation; the incompatibility in S_A solutions is promoted by an increased difference in the layer thicknesses of the components of the mixture. The second major result of this work is the evidence for different types of S_A–S_A consolute points.

A good linear correlation with the structures of the layers is observed when the two components are slightly and progressively modified within the series of homologues, but it cannot be extended to systems of very different type. The reliability in the calculation of the interaction parameter using Fedor's method might not be sufficient, as the ΔT parameter chosen to compare the behaviour of homologous systems fails to be a meaningful quantity when more important changes are introduced in the molecular structure of both components. It is also true that the influence cannot be analyzed in this work of other parameters such as localized steric hindrance of the perfluorinated parts within a layer or the elasticity modulus of the layers which is known to vary when the in-layer molecular packing is modified. However, evidence for unclearly identified interactions is given by the fact that the critical composition of the S_{A1}–S_{A1} system departs significantly from the regular solution model, behaving as if the volume fraction of the fluorinated compound were much larger than actually estimated (let us remark that in this case both

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[†] In order to compare with the theoretically expected critical compositions obtained from equation (3) in the text, we transformed the experimental data from molar fractions (x) to volume fractions (φ) using the molar volumes previously calculated (see table 4).

[‡] One can even imagine that a sufficient amount of **A** would destroy the layers, which is actually observed if **B** is just slightly shortened, as noted above.

ends of the molecule bear bulky perfluorinated segments).

We have also demonstrated that a polar component is not a required condition to produce phase separation. At this stage, the description of a system not involving a fluorinated mesogen and for which the incompatibility would be mainly based on a simple difference in layer spacings would be welcome. Our future investigations will aim at this result. Improving our knowledge in this way would require us to find new miscibility gaps for systems with varying molecular structures, although the example of the S_{A1}–S_{A1} system shows how the number of observable consolute points can unfortunately be limited.

Finally, it is important to highlight the fact that the critical temperatures of most of the systems described in this paper ensure thermal stability over long periods and easy temperature control, making them really convenient for additional physical investigations. We are currently performing high resolution X-ray scattering experiments and heat capacity measurements on F_4H_4 10OCB critical mixtures in order to establish the critical exponents which would help assign the universality class to which this critical point belongs [11].

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