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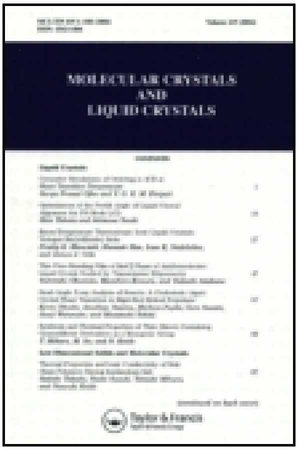

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Studies on Smectic Phase Inductions, IX. Anisotropic Solvation in 2D-Liquids

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Studies on Smectic Phase Inductions, IX. Anisotropic Solvation in 2D-Liquids†

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(*Received July 19, 1984*)

The influence of molecular length, structure and concentration on the induction of smectic phases in binary mixtures has been studied by thermal-, spectral-, X-ray- and dielectric methods. The enhancement or depression of the transition temperatures as well as other properties of high temperature smectic phases S_A, S_C and S_{Ad} have been treated within the framework of the anisotropic solvation or 2DS-model.

INTRODUCTION

Because, in terms of classification schemes, models for the induction of S_A phases were inconsistent with available data,[1] a two-dimensional solvation model was proposed[2a] and has been tested in different binary systems.[2b-2h] Some of the results are summarised here and treated within the 2DS-model which is then compared with other possible classification schemes.

MATERIALS AND METHODS

The molecular structure of the components studied can be characterised as:

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†Paper presented at the 10th International Liquid Crystal Conference, York, 15th–21st July 1984.

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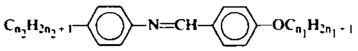
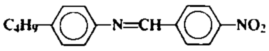
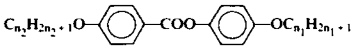
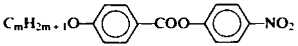
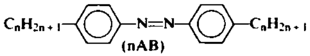
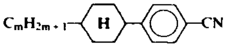
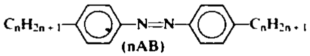
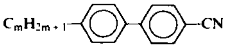
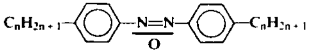
TABLE I

Components of the binary mixtures, with system-codes nSm./*N*: nematogen, *A*: smectogen/

Type	System	Component *1*	Component *2*	(Ref.)
N—(A—)	$\underline{n_1/n_2 04}$			[2a]
N—N(A—N)	$\underline{\tilde{n}_1/\tilde{n}_2 E\tilde{m}}$	 $(\tilde{n}_1/\tilde{n}_2PB)$	 $(\tilde{m}NB)$	[2g]
N—N	$\underline{nHm}$	 (nAB)	 (mCHB)	[2d]
N—N	$\underline{nIm}$	 (nAB)	 (mCB)	[2d]
N—N(A—N)	$\underline{n\dot{I}m}$	 (nAOB)	mCB	[2d]
N—N(A—N)	$\underline{\tilde{n}J\tilde{m}}$	ñAOB	m̃CB	[2d]

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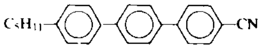
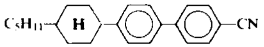
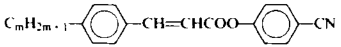
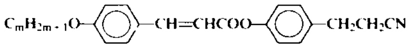
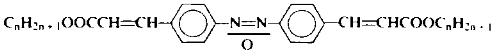
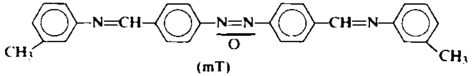
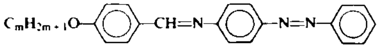
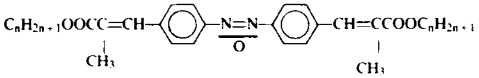
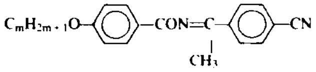
N—N(A—N)	<u>ṅT5</u>	ṅAOB		[2d]
N—N(A—N)	<u>ṅZ5</u>	ṅAOB		[2d]
N—N(A—N)	<u>ṅCm</u>	ṅAOB		[2]
N—N(A—N)	<u>ṅCm</u>	ṅAOB		[2]
A—A	<u>nNo</u>	 (nAOC)	 (mT)	[4]
A—A	<u>nMṁ</u>	nAOC	 (ṁM)	[2h]
A—N	<u>nWṁ</u>	 (nAOmC)	 (ṁW)	[2f]

1) *p*-,*p*′-dialkyl compounds with a *C*- number *n* in both end-chains:

$$\begin{array}{c} R_n\text{—}\boxed{\text{core}}\text{—}R_n \\ \leftarrow l_n \rightarrow \\ \longleftarrow L_n \longrightarrow \end{array}$$

2) compounds with no alkyl chain in one or both para-positions, with or without a strong terminal polar group:

$$\begin{array}{c} R_m\text{—}\boxed{\text{core}} \\ \leftarrow l_m \rightarrow \\ \longleftarrow L_m \longrightarrow \end{array}$$

L and *l* refer to molecular lengths (see below). For example, without R_m; $l_m = L_m$.

The system-code contains these *C*-numbers as: *nSm* (Table I). (From both compound-types nematogens, *N*, as well as smectogens, *A*, can be selected. $\bar{n}$ means an alkyloxy instead of an alkyl chain.) The smectic phase transition temperature, T_A, in binary mixtures of different homologous series (marked with capital letters in the *nSm* system-code) was measured by DSC or by polarising microscope equipped with a hot-stage as a function of the concentration (Figure 1). In binary mixtures of *x* mole fraction of component *2*,

$$X = (x)_{\max} \tag{1}$$

was the concentration at which the deviation from the additivity rule for T_A was found to be the greatest, or at which $(T_A)_{\max}$ could be detected, i.e., $T_X = (T_A)_{\max}$.
With

$$\overline{xT_A} = (1 - x)T_n + xT_m, \tag{2}$$

and

$$\underline{XT} = (1 - X)T_n + XT_m, \tag{3}$$

where $\overline{xT_A}$ is a straight line connecting T_n and T_m, and the line gives the S_A phase transition temperatures at different concentrations in a *nSm* system, and $\underline{XT}$ is a point on $\overline{xT}$ at $X = (x)_{\max}$ in (Eq. 3) (Figure 1b).

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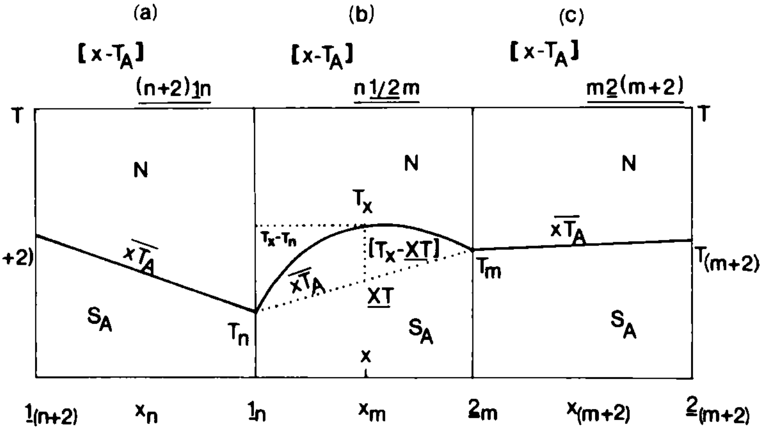

FIGURE 1 Schematic isobaric phase diagrams of homologues of components *1* and *2* in binary mixtures: ((a) and (c)) members of similar homologues, (b) members of different homologues.

In smectogen – smectogen, i.e., *A*-*A* binary systems

$$T_{IND} = T_X - \underline{XT} \tag{4}$$

can be the measure of induction.

In *N*-*A*, or *N*-*N* systems if one or both components are nematogens, Eqs. (2–4) can not be applied. The enhancement of T_n due to the addition of a second component in an *N*-*A* system of *X* mole fraction (Eq. 1) is calculated as

$$T_{IND} = T_X - T_n. \tag{5}$$

In the case of *N*-*N* systems, with no enantiotropic smectic phase of any of the components, the temperature T_X (in °C) was used in the calculations

$$T_{IND} = T_X. \tag{6}$$

The lengths of the molecules, *L*, and of their core, *l*, were measured on calotte models from end to end of their all-trans conformers. (In comparison, either the lengths *L* should be equal, or the length-ratio, *r*, should be greater than the saturation ratio, r_{sat}, in Eq. 11.)

In the concentration range $0 < x < 0.5$, the layer spacing values

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TABLE II

Influence of the concentration on the properties of binary mixtures of similar –, or different homologues of smectogens.

Systems	Methods	Properties	The rule of additivity in mixtures of similar-,	different- A-homologues was	(Ref.)
all	small-angle X-ray scattering	d (Eq. 7)	valid	valid ($0 < x < 0.5$)	[2]
all	polarising microscope	T_A (Eq. 2)	valid	not valid: T_X at $X = (x)_{max}$	[2]
all	DSC	ΔH_A	valid	not valid $(dH)_{max}$ at $x >$ 0.15	[2]
$\underline{\bar{n}\mathrm{I}\bar{m}}$	static dielectric permittivity	δ''_{NA} (Eq. 10)	valid	not valid: $(\delta''_{NA})_{max}$, $x > 0.15$	[2e]
$\underline{n\mathrm{I}m}$	FTIR	ν^*_{NA}	valid	not valid: low-frequency shift of $(\nu^*)_{CN}$ at X	[2c]
$\underline{n\mathrm{I}m}$	UV-FTIR	spectra (200–50.000 cm^{-1})		no CT-band was detected	[2c]

measured by small-angle X-ray diffraction fulfilled the rule of additivity in all systems studied,

$$d = (1 - x)L_n + xL_m = \overline{xL} \tag{7}$$

neglecting small deviations due to thermal fluctuations around the director.[3]

The influence of L on T_{IND} was studied. As a means of comparing systems containing different cores and end-chains and to make comparisons with incommensurability data of the single components, the ratio, r, of the molecular lengths was used in the form

$$r = \frac{\underline{XL}}{L_m}, \tag{8}$$

where

$$\underline{XL} = (1 - X)L_n + XL_m. \tag{9}$$

$\underline{XL}$ means the layer distance of the induced S_A phase at X ($\underline{XL}$ is a point on the $\overline{xL}$ line).

The change of the static permittivity at the N-A phase transition could be characterised by

$$\delta''_{NA} = 1 - \frac{\min\epsilon_{\parallel}\ (\text{in } S_A)}{\epsilon_{\parallel}\ (T = T_A)} \tag{10}$$

while IR spectral changes concerning either the CN-group frequency or the frequencies of the aromatic part were characterised by the high- or low-frequency shifts detected by ratio-recording FTIR or by the spectral subtraction technique.

RESULTS

Different properties of the components were measured both in their single component A or N phases and in mixtures. Comparisons were made using data measured either at constant temperature or at fixed concentration.

I. Table II summarises the results concerning *the influence of the concentration* in mixtures of homologues whose lengths were not very different (as in Figure 1a, 1c), and in mixtures of different homologues

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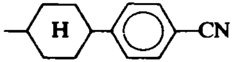
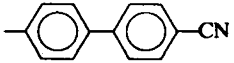
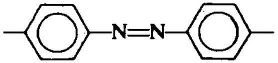
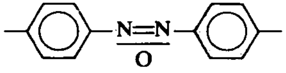
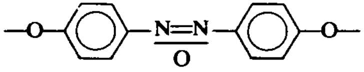
TABLE III

Influence of the structure of the components' core on $T_{IND}/L_n >> L_m/$

System	Cores in question		T_{IND}	(Ref.)
nH5	nAB +		59.5°C	[2d]
nI5			66.5°C	[2d]
nI5		+ 5CB	66.5°C	[2d]
nĪ5			79.0°C	[2d]
n̄Ī5			124.5°C	[2d]

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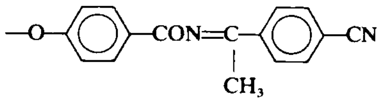
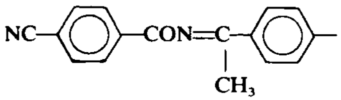
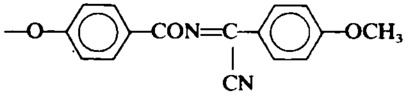
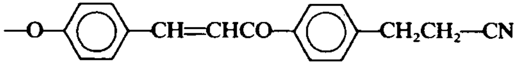
nW$\bar{9}$	nAOmC +		35°C	[2f]
niW9			15°C	[2f]
—			0°C	[2f]
n̄C̸m̄	n̄AOB +		0°C	

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($L_n \gg L_m$) (Figure 1b). For example, the properties of the *nAB* or the *mCB* homologues in their mixture (as in Figures 1a and 1c) followed linearity whereas in their mixtures, *n*/*m*, deviations from the additivity rule were detected (as in Figure 1*b*). All of the properties in Table II except *d* exhibited deviations from the additivity rule. Maxima could be detected at $x > 0.15$, from a 6:1 molecular ratio.

II. *The influence of the length of the molecules* can be summarised in the following way (Figure 2). If $L_n > L_m$ and $l_n = l_m$, T_{IND} values reached saturation (T_{IND} were calculated according to Eqs. (4–6)). T_X, as well as T_{IND} saturation values of a system, depend on the structure of the components' core, i.e. dipoles, conjugation length, the orientation of strong dipoles, etc. (see Table III), or on the alkyl chain length of component *2*.

The induction of the S_A phase was depressed in all cases when the *ratio of the molecular length, r,* was smaller than a characteristic value of *r*, r_{sat}. It was proved in different systems that:

$$r_{sat} L_m = d_m, \text{ if } r_{sat} = r_d, \tag{11}$$

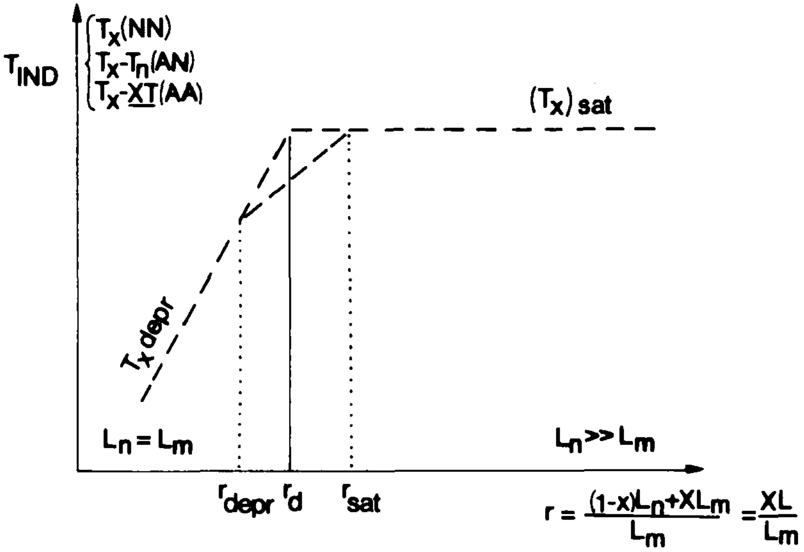

FIGURE 2 $T_{IND} - r$, induction vs. length ratio diagram of binary systems (schematic illustration).

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or

$$r_d L_m = d_m, \quad \text{if an intermediate slope is present.} \qquad (12)$$

This means that r_d is a property of component *2* as well as d_m, and that it is the limiting molecular ratio, if $r_d = r_{sat}$, in binary mixtures under which only the depression of T_X could be detected (Table IV). Other properties of the $r - T_{IND}$ saturation curves such as the appearance of an intermediate slope connecting the saturation and the depression lines, the even-odd effect yielding even and odd r_{sat} values, or the decrease of the $(r_d)_m$ values within a homologous series with increasing L_m were discussed in reference 2d. (When the $r - T_{IND}$ curve contains an intermediate slope the extrapolated r_{sat}-value, r_d in Figure 2, should be used for comparison with d_m.) Figure 3 shows a complete $r - T_{IND}$ curve with the above mentioned characteristics; r and $T_{IND} = T_X\text{-}\underline{XT}$ values were calculated using the xT_A-data of reference 4 (system *nNo*, Table V).

DISCUSSION

Structural asymmetries and other properties of the components exhibiting induced smectic phases in binary mixtures, and the requirements of quasi-hexagonal close-packing of such species in a 2D-liquid were taken into consideration in the anisotropic solvation, or 2DS-model.[2a] If one wishes to form a solvate in a binary mixture of two compounds, characterised by *1* and *2* in the MATERIALS AND METHODS section, the only requirement is that they have to exhibit a suitable and sufficient difference of their rigid, mainly aromatic, and their flexible aliphatic segments. Such properties of the components as:

- terminally polar + nonpolar, P/N, or
- double-layer forming + nonlayered, D/M, or
- compounds with strong donor and acceptor properties exhibiting charge-transfer in their mixture, CT,

are not required. These might characterise different subclasses which may well belong to the phenomenon, but they can be used only with limitations.

For example, the components of the system *nNo* (*nAOC* and *mT* in Table I) are azoxybenzene derivatives without strong donor-ac-

TABLE IV

Comparison of the layer distances, d_m and r_dL_m/see text/

Compound	d_m (nm)	(Ref.)	System	r_dL_m (nm)	(Ref.)
5CB	2.51	[2b]	$\underline{\text{nI5}}$	2.49	[2d]
5CHB	2.63	[5]	$\underline{\text{nH5}}$	2.62	[2d]
$\bar{9}$W	3.40	[2e]	$\underline{\text{nW}\bar{9}}$	3.42	[2f]
$\bar{8}$NB	2.96	[6]	$\underline{\bar{\text{n}}_1/\bar{\text{n}}_2\text{E}\bar{8}}$	2.91	[2g}

ceptor properties, they are not double layer forming materials[7] and, finally, they have no strong terminal polar group on either of them. Therefore S_A induction should not have been exhibited in their mixture according to P/N, D/M or CT classifications. Nevertheless, strong S_A induction, together with S_C enhancement were detected in *nNo* systems.[4] As to the 2DS-model, the non-additive enhancement of T_A of component *1* due to the addition of *2* should be the consequence of weak, van der Waals–London, intermolecular interactions. The solvates to be formed can only be anisotropic because like segments of the different molecules surround each other, i.e. flexible segments surround flexible ones, rigid segments rigid ones. Therefore, the diameter of the solvate can be increased only in the *x*-*y* directions whereas their length along the *z*-axis either (i) remains constant, depending on the concentration (hetero-solvation in mixture), or (ii) depending on the temperature, has a fixed incommensurable length, d_m, compared with L_m (homo-, or auto-solvation in single component

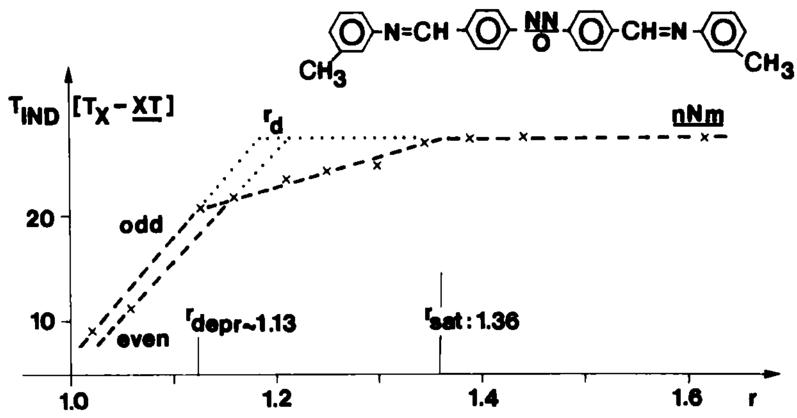

FIGURE 3 T_{IND} – *r* diagram of *nNo* system: *n*-alkyl azoxycynnamates, *n* = 2–16, were mixed with azoxybenzilidene meta-toluidine (after Reference 4).

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TABLE V

T_{IND}-r date of the nNo system./Calculated after Ref.4

n:	3	4	5	6	7	8	9	10	11	12	16
$r = \frac{XL}{L_m}$:	1.02	1.06	1.12	1.16	1.21	1.25	1.30	1.35	1.39	1.44	1.62
$T_X - \underline{XT}$:	9	11	21.1	22	23.7	24.4	24.8	27.1	27.7	27.8	27.5

S_{Ad} phases, with molecular dipoles oriented antiparallel within the solvate).

Hetero-solvation has been proved by DSC: Broad maxima between $x = 0.15$ and $x = 0.4$ were measured for S_A-N (S_A-I) transition enthalpies (in the $\overline{6}/\overline{10}E\overline{8}$ system,[2a] and the 7I5 system, respectively).[2d] The 6:1 molecular ratio at $x = 0.15$ seemed to be the concentration at which the first complete solvation shell could be built around component *2*, without excess *1* in a quasi-hexagonal 2D-close-packing arrangement (Figure 4a). Further addition of component *2* provided only minor enhancement due to stronger coupling between building units (solvates, possibly in a shared-shell packing). It was found by DSC that this 2:1 molecular ratio was the most favourable for S_B induction.[2b] The 1:1 ratio, preferred for S_E,[2b] showed no difference concerning interaction.

Figure 4 is a schematic illustration of probable packing in a 2D-

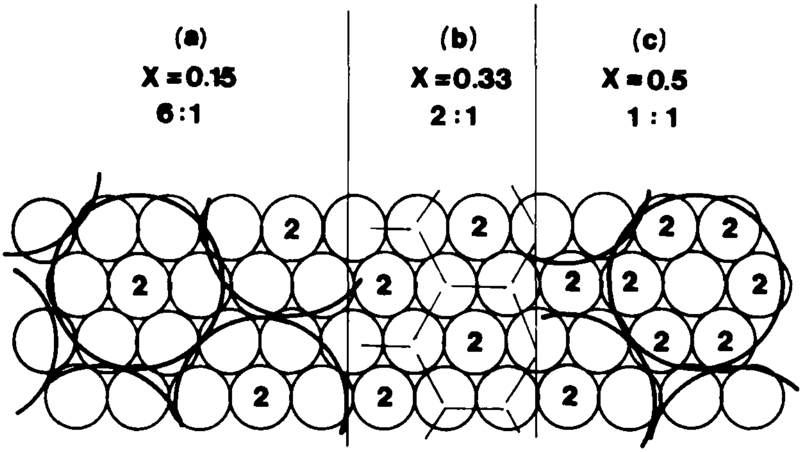

FIGURE 4 Schematic arrangements of components *1* and *2* in a 2D-layer at different concentrations: at (a) 6:1; (b) 2:1; and (c) 1:1 molecular ratios.

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layer at different concentrations. It should be noted that in nature there must always be a considerable disorder because of the liquid state.

If the symbols i.e. the circles with the 2 and the empty circles, (Figure 4c), indicate opposite orientation of terminally polar molecules along z then it would be possible to characterise the S_{Ad} arrangement by antiparallel homo-solvates mixed with unsolvated molecules. (Calculations based on the Ising-model have hinted hexagonal packing.[8])

With decreasing mole fraction of *2* a continuous variation of homo- and hetero-solvates, the latter are inverted in this concentration range in relation to the 6:1 solvates, has been indicated by static permittivity measurements made both in S_{Ad} and in the induced S_A phase.[2e] The similarity of $d_m = r_d L_m$ (Eqs. 11 and 12) also support this concept (Table IV).

The separation of hard and soft segments of the molecules forming thermodynamic subsystems is in agreement with earlier proposals based on X-ray studies on (cybotactic) nematic and mesomorphic polymer phases.[9]

The depression of T_X due to shortening of the "layer" distance in the mixture is no doubt the result of the asymmetric packing of component *2* along the z direction in the 2D-liquid. Studies of $T_X - r$ diagrams have suggested the validity of the additivity rule concerning not only L in Eq. 7 but the core-length, l, also[2d]

$$\overline{xl} = (1 - x)l_n + xl_m \tag{13}$$

if one assumes "separated" subsystems of the rigid and flexible segments of the molecules coupled to each other ("demixing" into the S_A phase[9c]). The xy interaction (attraction) length should depend on the concentration, if $l_n \neq l_m$, following the reduction of the $\underline{XL}$ "layer" distance, (Figure 5).

The unidirectional repulsion along z would disrupt and subsequently cause disintegration of some or all the solvates depending on the degree of shortening of $\underline{XL}$.

SUMMARY

The components of a binary mixture—given a suitable and sufficient difference between their cores and end-chain asymmetries—can be integrated into quasi-hexagonal solvates at a higher temperature than

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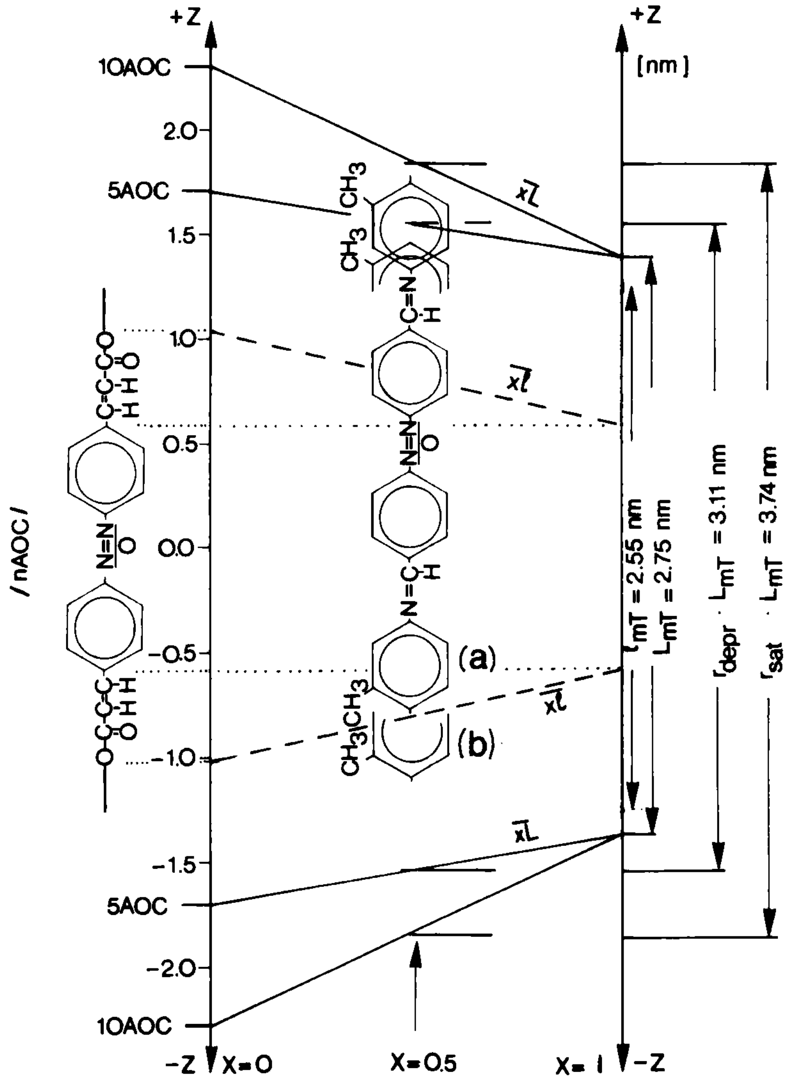

FIGURE 5 Mean values of the "layer" distances, $\overline{xL}$ and $\overline{xl}$, vs. concentration; (a) *nNo* system at $r < r_{sat}$; and (b) $r < r_{depr}$.

either T_n or T_m. As a consequence of the greater inertia of these entities, or the lowered enthalpy of the system, the S_A phase transition temperature should be increased if steric hindrance along the z axis and attraction within the xy plane are in favourable equilibrium. The depression of T_X should then be a result of changing this equilibrium.

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