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Liquid Crystals

Publication details, including instructions for authors and subscription information:

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To cite this Article Dabrowski, R. , Czupryński, K. , Przedmojski, J. and Ważyńska, B.(1993) 'Creation of nematic and reentrant nematic phases in bi- and multi-component smectic mixtures', *Liquid Crystals*, 14: 5, 1359 – 1369

To link to this Article: DOI: 10.1080/02678299308026448

URL: <http://dx.doi.org/10.1080/02678299308026448>

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Creation of nematic and reentrant nematic phases in bi- and multi-component smectic mixtures

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Experimental results referring to the transformation of smectic phases, mainly smectic A, into nematic and reentrant nematic phases are reviewed. A new explanation of some experimental results is proposed. Factors which are responsible for the depression of smectic phases in mixtures of polar mesogens are discussed and the possibility of forming mixtures with a broad temperature range of nematic phase from smectic compounds, which can be useful for liquid crystal displays (LCDs), is shown. A nematic gap observed in some cases between monolayer (S_{A_1}) or monolayer and partially bilayer (S_{A_d}) smectics results from the differences in the organization of the molecules in the smectic layers. It is concluded that polar phase from smectic A_1 phases can be divided into two groups: (a) the first one is characteristic for compounds with the $-NCS$, $-F$, $-Cl$, $-I$ or $-COC_mH_{2m+1}$ terminal group. The spacing of the smectic layer slowly expands with the increase in alkyl chain length and the structure of the smectic A_1 phase slowly changes to be more like the smectic A_d phase ($d/l > 1$). It is proposed that such a smectic is called an enhanced monolayer smectic (S_{A_1e}); (b) the second one is typical for compounds with the $-CN$ terminal group. This kind of smectic A_1 phase is rapidly transformed into the smectic A_d phase with increasing alkyl chain length. These latter monolayer mesogens easily form the reentrant nematic phase when they are mixed with other polar smectic mesogens.

1. Introduction

For a number of years we have been investigating the creation of nematic phases from smectic compounds and have found that it is possible to obtain mixtures with a normal nematic phase existing over a broad range of temperature and concentration from mesogens having only smectic phases [1-9]. We proposed the term 'the nematic phase created by depressing the smectic stability' for such an effect [4]. The creation of a nematic phase for a closed region of temperatures and concentrations has also been observed several times by Sackmann, Demus and their co-workers [10-12]. They termed this 'a stabilized intermediate nematic phase' and suggested that it arises from a hypothetical thermodynamically unstable nematic phase of one or both components. In this paper we will summarize our experimental results referring to formation of such nematic phases as an example of the more general problem concerning the transformation of more ordered phases into less ordered ones and we will give a new explanation of such behaviour. The transformation of polar smectic A systems into nematic phases (see figure 1 (a)) has been extensively investigated by ourselves. We have also observed the transformation of the smectic C phase into the nematic [13] or smectic A [14] phase (see figure 1 (b)), the smectic B into the smectic A [15] (see figure 1(c)) and the smectic E into the smectic A [16] phase (see figure 1 (d)).

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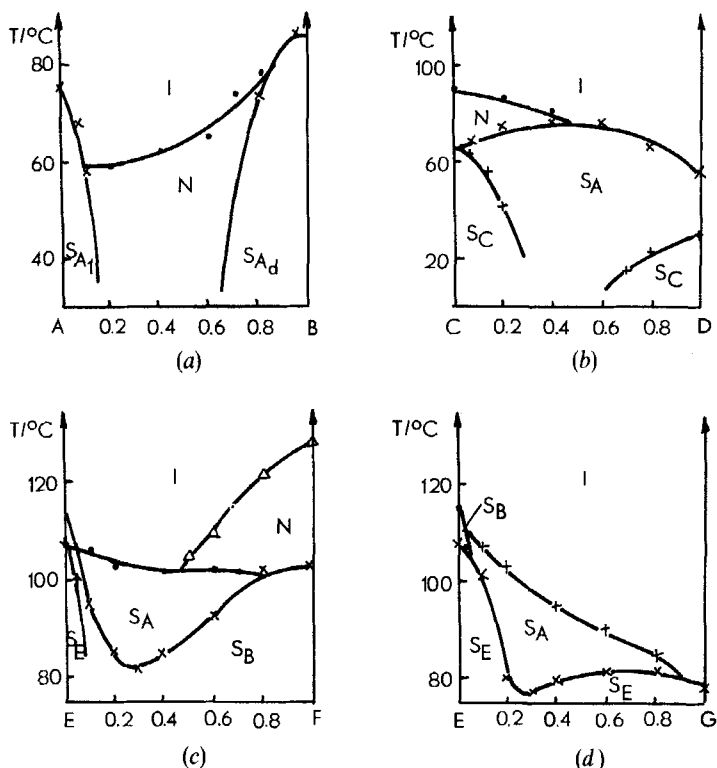
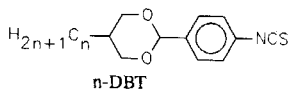


Figure 1. Phase diagrams showing the transformation of the more ordered liquid crystal phases into less ordered ones where A is 2-(4-isothiocyanatophenyl)-5-butylidioxane-1,3, B 4-cyanophenyl 4-dodecyloxybenzoate, C 4-hexyloxyphenyl 4-octyloxybenzoate, D 4-(2-methylbutyloxycarbonyl)phenyl 4-octyloxybenzoate, E 4-pentyl-4-pentanoyloxybiphenyl, F 1-(4-octylbiphenyl-4')-2-(4-isothiocyanatophenyl)ethane and G 4-dodecyl-4'-acetyllobiphenyl.

2. Destabilization of smectic A phases in mixtures

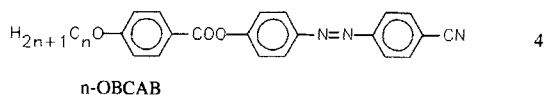
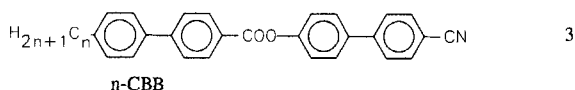
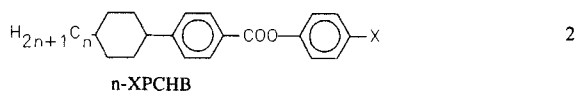
2.1. A_1 - A_1 Systems

The simplest systems, wherein creation of a nematic phase is observed, are bicomponent smectic A_1 mixtures containing members of the same homologous series, for example the compounds of formula 1:



The first mixture in which the nematic phase appears over a narrow temperature range in the central region of concentration is 4DBT-7DBT (layer spacing ratio $d_7/d_4 = 1.23$) and is systematically enhanced for the next members, and for 4DBT-12DBT, ($d_{12}/d_4 = 1.69$) the nematic phase exists for a range of 15° (see figure 3 in [4]). In the mixture 4DBT-10TPCHB (10TPCHB, formula 2, $X = -\text{NCS}$, $n = 10$) the smectic A phases of both components are fully separated by a nematic gap. It was suggested that a growing difference between the smectic layer spacing of the components is mainly responsible for this behaviour [4], but we will show later that this point of view must be

partially revised. In binary mixtures containing n -XPCHB ($X = -\text{NCS}$, $-\text{I}$, $-\text{F}$, $-\text{COCH}_3$ and $n > 7$; n is the number of the carbon atoms in the alkyl chain) and one compound chosen from homologous series 3 wherein $n \leq 7$ or from homologous series 4 wherein $n \leq 8$, one of us [17–20] observed that two smectic A_1 regions are separated by a nematic gap or a nematic gap which accompanies a reentrant nematic phase and the reentrant nematic phase is moved to larger concentrations of the compound n -CBB or n -OBCAB



as the alkyl chains grow, see for example figure 3 in [17], but on the other side these compounds are miscible nearly additively or a shallow minimum is observed, when the following a or b conditions are fulfilled:

	a	b
n -XPCHB	$n > 7$ or	$n < 8$
n -OBCAB	$n > 8$ or	$n < 9$
n -CBB	$n > 7$	$n < 8$

Compounds n -CBB [20] and n -OBCAB [21] belong to those homologous series which have the monolayer smectic A_1 phase and a nematic phase for members with alkyl chains shorter than octyl or nonyl, respectively, or S_{A_1} , N_{re} and S_{A_d} phases for longer alkyl chains. The observed miscibility confirms that the symmetry and structure of the smectic layers of the compounds n -XPCHB is more similar to the layer structure of cyano compounds with monolayer ordering when the alkyl chain is shorter and resembles their partially bilayer structure (A_d) when the alkyl chain is longer. To understand this behaviour better we have measured the layer spacing for TPCHB compounds ($n = 4$ – 12) by X-ray diffraction and these results, together with those previously obtained for DBT ($n = 4$ – 12), are plotted in figure 2. The comparison of the layer spacings d to the length of the molecules l in the most stretched all-*trans* configuration shows that the layer spacing is enhanced when the alkyl chain length is increased. The ratio d/l changes from 0.88 to 0.99 in the n -DBT series and from 1.0 to 1.09 in n -TPCHB series. In the former homologous series, d approaches l for the large n , but for the latter series, d moves away quickly from 1 for large n . This suggests that the internal structure of the smectic layer must change and that this happens in a continuous way. The differences in the internal structure between the first and the last members of the same homologous series are not high, because their smectic A phases

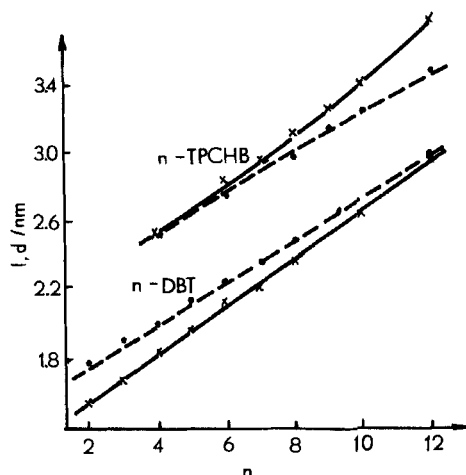


Figure 2. The experimental values of the layer spacing d in the n -DBT and n -TPCHB homologous series (continuous lines) and the calculated length of the molecules in the most stretched all-*trans* configuration (dashed lines).

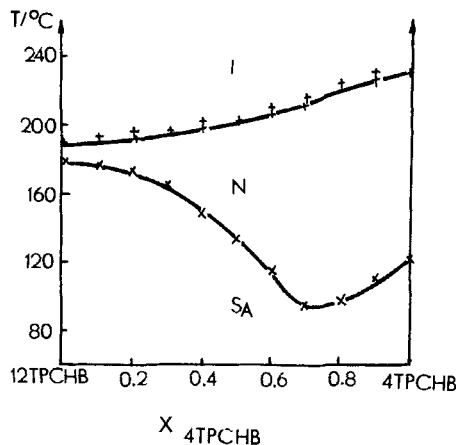


Figure 3. Phase diagram of the binary system 4-TPCHB-12TPCHB.

are fully miscible; only a small minimum in the S_A -N transition curve is observed, see figure 3. The differences in the internal structure of the smectic layers between the first member of the n -DBT homologous series and the last member of the n -TPCHB series are large enough to break the miscibility completely, and the nematic gap separating two smectic regions occurs.

Gramsbergen and de Jeu [26] investigated the molecular organization on the free surface of polar monolayer smectics (S_{A_1}) with $-\text{CN}$ or $-\text{NCS}$ terminal groups and have found that an isothiocyanato compound (compound 7TPCHB was investigated, $d/l = 1.01$; 1.02 is our result) has a molecular organization exhibiting random up and down orientations of the molecular dipoles in the layer, as in the classical smectic A_1 phase while cyano compounds have layers in which the dipoles are strongly correlated. The molecular organization resembles the bilayer S_{A_2} structure.

The ratio of up to down oriented molecules in the smectic layers of the isothiocyanato compounds is not fixed, but should change as the length of the alkyl

chains changes because the conditions of the equilibrium between steric repulsive forces and intermolecular attractive forces are changing. Theoretical calculations made by Longa and de Jeu [27] show that longer molecules easily associate to form dimers with terminal group dipoles oriented in the opposite direction (local antiferroelectric order), than shorter molecules. Also the calculations made by Madhusudana showed that pairs of molecules with parallel oriented dipoles (ferroelectric short order) may be formed only by molecules with short alkyl chains or at lower temperatures [28]. Taking into account these results, we suggest that the smectic A phase of n -DBT and n -TPCHB compounds consisting of molecules with a short alkyl chain have an order similar to the ferroelectric order and it is more strongly exhibited in the n -DBT layers than in the n -TPCHB layers, because the first compounds are more polar. The increase of the alkyl tail length favours the antiferroelectric order that leads to the classical randomly ordered smectic layers for $n=6-8$ and then for greater n , when a dimerization occurs, a slow change of the smectic A_1 layer into a layer resembling the S_{A_d} type is observed. Such behaviour is characteristic not only for polar compounds with $-NCS$ terminal group, but for compounds with other terminal groups, such as $-F$, $-Cl$, $-I$, $-COCH_2H_{2m+1}$.

In order to distinguish such a smectic A phase with the ratio $d/l \geq 1$ from the classical smectic A_d with the ratio $d/l = 1.4$ and to underline that the former is formed by a progressive expansion of the monolayer, we propose to term it the enhanced monolayer smectic A ($S_{A_{1e}}$).

The compounds n -XPCHB show not only a growing tendency to dimerize when alkyl chains increase, but they also have a strong ability to invoke the dimerization of compounds with $-CN$ terminal groups having a shorter alkyl tail ($n < 8$) such as n -CBB or n -OBCAB or compounds similar to them [19, 23]. Hence their partially virtual bilayer properties came to light.

The n -CBB or n -OBCAB compounds find better conditions for dimerization in the $S_{A_{1e}}$ phase rather than in their own S_{A_1} phase. This is concordant with Longa and de Jeu's theoretical model. This model postulates that both monomers and dimers are necessary to form a stable smectic A_d phase, because the space is filled better than in the case when a dimer is only surrounded by dimers. Induced forces between dimers, monomers and between dimers and monomers stabilize the smectic A_d phase and the layer spacing for the more suitable conditions of these interactions becomes equal to the length of a dimer. The $S_{A_{1e}}$ matrix of XPCHB compounds contains a small number of its own dimers which are not able to form the smectic layer of the dimer length, although the alkyl chains are long the intermolecular associative forces are not large enough. Such conditions facilitate the dimerization of the n -CBB or n -OBCAB molecules which have a stronger ability to dimerize. Probably all of the n -CBB or n -OBCAB molecules transform to dimers. This allows us to obtain the more optimal ratio of dimers to monomers needed for the layer spacings to be equal to the length of dimers. Only molecules with $-CN$, $-NO_2$ and $-CHO$ terminal group are able to form directly the smectic A_d phase [5]. The dipole moment of the $-CHO$ group is smaller than that of the $-NCS$ group, and therefore it seems that not only the induced forces as Longa and de Jeu suggested [27], but also other types of intermolecular forces such as donor-acceptor intermolecular forces must participate in the dimerization.

X-ray diffraction studies show that the experimental layer spacings of the above mentioned n -CBB-XPCHB or n -OBCAB-XPCHB mixtures increase with the concentration of the cyano component. They are greater than the values calculated from the spacing of the pure components, but they are concordant with the assumption that

the cyano component forms dimers with antiparallel oriented molecules and in which the overlapping of the rigid core of the molecules occurs [23, 24]. For example at 130°C in the mixture $X_{7\text{CBB}} = 0.7$ and $X_{10\text{XPCHB}} = 0.3$ ($X = \text{COCH}_3$) $d = 3.77$ nm was measured; the value calculated from the data of the pure compounds was $d = 3.45$ nm, but $d = 3.75$ nm when 7CBB is taken as the dimer. This gives direct evidence that in the mixture, the dimers are formed and this is the reason why the reentrant nematic phase in the mixture composed formally only of monolayer compounds (smectics A_1 and A_{1e}) is observed. According to the model of Longa and de Jeu, the dimers are stable only in a certain range of temperatures. On decreasing temperature increases repulsive steric forces and a nematic phase is favoured once more.

2.2. A_1 - A_d systems

Polar monolayer smectic A_1 phases are miscible with partial bilayer smectic A_d phases when the alkyl tail is long (according to the proposed notation they are $S_{A_{1e}}$) and are immiscible when the alkyl tail is short. A very broad nematic gap fully separating two smectic regions may be observed [1-3, 5, 7]. The smectic A_d phase is observed for pure compounds with long alkyl tails, usually with $n \geq 8$, except for example in the series 2-(4-*trans*-4-alkylcyclohexylphenyl)-1-cyanoethene (*n*-EPCH) in which the smectic A_d phase is observed for $n = 4$. A complete separation of the smectic A_d and smectic A_1 regions by a nematic gap takes place when the alkyl chain in the smectic A_1 phase is heptyl or shorter. A nematic gap shorter or broader may be observed for every pair of bi-ring compounds shown below when one component of a mixture is taken from the compounds listed in the left hand column and another from the compounds listed in the right hand column of table 1. The nematic gap was also observed for mixtures containing three ring components, but only the limited number of such systems listed below has been investigated thus far, see table 2.

Table 1. Bi-ring compounds giving the nematic gap in the S_{A_1} - S_{A_d} bicomponent systems

Smectic A_1	Smectic A_d
$n < 8$	$n \geq 8$
	$n \geq 10$
	$n \geq 4$

Table 2. Three ring compounds giving the nematic gap in the S_{A_1} - S_{A_d} bicomponent systems.

Smectic A_1	Smectic A_d
	$n \geq 9$

If the above mentioned smectic A_1 and A_d compounds are mixed with each other, the reentrant nematic phase is usually observed on the side of the smectic A_d component, but usually over a short range of concentrations [3, 6]. Other behaviour is observed if the monolayer smectic A belongs to the homologous series n -CBB, formula 3 or to series with similar properties, many of which were described by French scientists [22]. These smectics A_1 when mixed with A_d smectics (for example with the compounds n -XPCHB, formula 2 when X is $-\text{CN}$, $-\text{NO}_2$, $-\text{CHO}$) give the diagrams showing that the stability of the smectic A_1 decreases strongly, but the stability of the smectic A_d phase is enhanced evidently as the alkyl chain length of the monolayer components increases and the nematic gap and the reentrant phase is created and moved to the side of higher concentration of the component with the smectic A_1 , see figure 6 in [5]. The monolayer members of the n -CBB series introduced into a matrix composed of smectics A_d reveal to an increasing extent the properties which are characteristic for S_{A_d} structures, as they are closer to the compound with the octyl chain. A hypothetical smectic A_d -nematic phase transition temperature may be estimated by extrapolation. It is interesting to note that phase diagrams of the mixture composed of n -CBB compounds ($n < 8$) and n -XPCHB compounds ($n \geq 8$) when $X = -\text{NCS}$, $-\text{F}$, and $-\text{COCH}_3$ (a) or $X = -\text{NO}_2$, $-\text{CHO}$, and $-\text{CN}$ (b) are very similar; compare figure 3 in [17] with figure 8 in [5]. The compounds (b) are typical smectics A_d with $d/l \sim 1.4$, whereas in the case of compounds (a) d is only a little higher than 1, but nevertheless it seems that their internal structure should be similar. Therefore we suggest calling them S_{A_1e} .

All the above mentioned bicomponent S_{A_1} - A_d systems, in which a nematic gap or with a nematic gap accompanying the nematic reentrant phase is observed, contain the compounds with a terminal polar group, which is placed in relation to the other polar group in the molecules in such a way that their dipole moments are concordant. This orientation of polar group dipoles seems to be very important for the possibility of depressing smectic stability. It was confirmed by the phase diagram study of isomeric cyanopyrimidines having the same shape molecules and the same layer spacing of the smectic A_1 phase but oppositely oriented dipole moments of their polar groups. Only in the case of the mixtures of smectics A_d with smectic A_1 cyanopyrimidines having their dipole moments oriented in the same direction a nematic gap is observed [6], but it is still difficult to say if this condition is necessary for all systems in which a nematic gap may occur.

The next very important parameter is the energy of the smectic layer formation. The smaller the enthalpy of the S_{A_1} -I or S_{A_1} -N phase transition observed for the pure components the wider is the nematic gap. Similarly, for the S_{A_1} -N second order phase transition, the lower the S_{A_1} -N phase transition temperature the broader is the nematic gap.

3. Phenomena accompanying the depression of smectic stability

A large decrease of the S_A -I phase transition enthalpy in the central range of concentration is observed for mixtures composed of less distant members of homologous series in which the nematic phase is still not observed [3-5]. In the mixture with a nematic gap, the introduction of the second component causes the enthalpy of the S_A -N transition to decrease quickly to zero and the S_A -N becomes a second order transition. The decay of the forces bonding the molecules in the smectic layer is the main reason why the hypothetical nematic properties of the smectic compounds are revealed. The values of the bulk viscosity of the nematic created in such a way are similar to the viscosities of normal nematic compounds of the same chemical classes. The viscosity changes with the concentration and has its lowest value in the central part of the nematic gap (4DBT-8OCB). Czupryński and Janik [29] have measured three different Mięslowicz coefficients for the 4TPB-8OCB mixture and found for $x_{8OCB} = 0.5$ that the following sequence

$$\eta_1(n_{\perp} V n_{\parallel} \Delta V) > \eta_3(n_{\perp} V n_{\perp} \Delta V) > \eta_2(n_{\parallel} V n_{\perp} \Delta V)$$

occurs. It is worth noting that this sequence is the same as that found in the case of the classical nematic 6CHBT [30] (see table 3). This means that smectic-like ordering in this nematic is completely destroyed and this is confirmed by the measured diffraction X-ray pattern. In all the concentration range of the mixtures containing S_{A_1} - A_d components only one internal reflection in the form of non-split spots is present. The spots are sharp for pure compounds and become diffuse for mixtures with a nematic gap, resembling the reflection pattern which is typical for poorly ordered nematics with a small correlation length of the smectic-like ordering. Simultaneously, the X-ray pattern shows that the change from the monolayer to the semibilayer structure has a threshold character and i.e. a rapid change is observed in a small concentration range. The change of the molecular dimensions is more drastic in the neighbourhood of the monolayer smectic A-nematic phase transition border than in the neighbourhood of the partially bilayer smectic A_d -nematic phase transition border [5]. The molar volume increases as a result of mixing in all the concentration range except for the small concentration range near to the pure A_d component (4DBT-8OCB system was investigated [7]). The greatest change in the mixing volume is observed at the side of the monolayer component. The changes of the molar value are rather big and are similar in the smectic phase and in the isotropic phase [7].

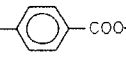
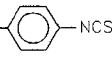
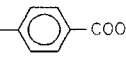
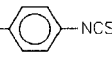
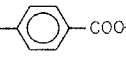
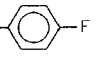
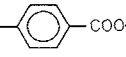
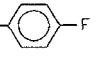
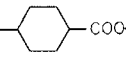
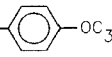
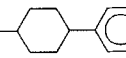
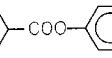
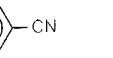
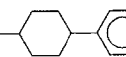
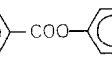
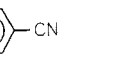
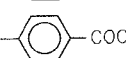
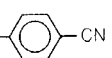
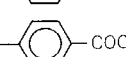
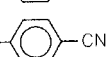
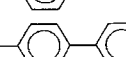
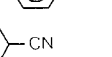
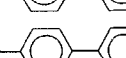
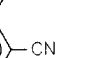
Table 3. The comparison of the viscosity coefficients of 6CHBT and the bicomponent mixture of 4DBT-8OCB with the mole ratio of $X_{8OCB} = 0.5$

Substance	$T/^{\circ}C$	η_1	η_3	η_2
4DBT-8OCB	38	83.6	28.2	22.7
6CHBT	20	93.0	28.0	12.0

4. Multicomponent nematic mixtures from smectic compounds

Using the previously mentioned rules for depressing the smectic stability in bicomponent mixtures, in the case of multicomponent smectic A mixtures, it is possible to obtain nematic mixtures existing over a large temperature range and with viscosity

typical for conventional commercial nematic mixtures. Figure 4 shows the phase diagram in which components M_{A_1} and M_{A_d} are the eutectic mixtures: the first one consisting of smectic A_1 compounds and one nematic compound and the second one consisting of the smectic A_d compounds. Mixtures M_{A_1} and M_{A_d} have the following composition (wt%):

M_{A_1}		
H_9C_4 —  —COO— 	19.5	
$H_{17}C_8$ —  —COO— 	34.0	
$H_{11}C_5O$ —  —COO— 	6.0	
$H_{13}C_6O$ —  —COO— 	9.8	
$H_{11}C_5$ —  —COO— 	30.7	
M_{A_d}		
$H_{21}C_{10}$ —  —  —COO— 	5.2	
$H_{17}C_8$ —  —  —COO— 	3.4	
$H_{25}C_{12}O$ —  —COO— 	3.4	
$H_{21}C_{10}O$ —  —COO— 	3.1	
C_8H_{17} —  — 	60.8	
$C_8H_{17}O$ —  — 	24.1	

The electro-optical properties of mixtures from figure 4 change strongly in relation to their position in the nematic gap. The mixture with the ratio M_{A_1} to M_{A_d} 1 : 1 by weight at 20°C has the properties shown in table 4. The mixture shows an excellent threshold steepness in a normal $\pi/2$ twist cell.

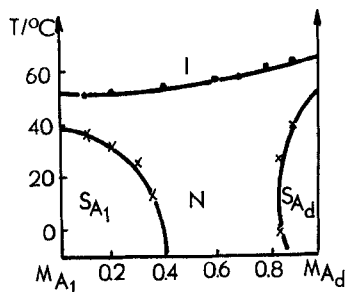


Figure 4. Phase diagram for the system composed of two multicomponent eutectic mixtures M_{A_1} and M_{A_d} .

Table 4. Properties of a mixture of mixtures M_{A1} and M_{Ad} in a 1:1 wt/wt ratio at 20°C.

V_{10}	1.53 V	η	38.2 mPa.s
V_{50}	1.65 V	$\Delta\epsilon$	10.35
V_{90}	1.93 V	$\Delta\epsilon/\epsilon_{\perp}$	1.8
V_{50}/V_{10}	1.08	Δn	0.167
V_{90}/V_{10}	1.26	n_0	1.513
T_{on}	56 ms		

5. Conclusions

Mesogenic compounds with a terminal polar group, with or without bridging groups in their structure and having all their dipole moments concordant may be divided into three groups according to their ability to form smectic A phases:

- compounds with terminal groups such as: $-NCS$, $-F$, $-Cl$, $-I$, $-COC_mH_{2m+1}$ form the monolayer smectic A phase; the layer spacing slowly expands with increase in alkyl chain length; this means that the internal structure of their layer is continuously transformed into the S_{Ad} -like structure. Such A_1 smectic, for which the ratio $d/l > 1$, we propose to term enhanced monolayer smectic A (A_{1e}),
- compounds with $-CN$, $-NO_2$ or $-CHO$ terminal group, where the polarity of the molecule as a whole is high, with moderation usually for $n \geq 8$, form the smectic A_d phase ($d/l \sim 1.4$) which is accompanied by the nematic and/or virtual reentrant nematic phases,
- compounds with $-CN$ or $-NO_2$ terminal group, where the polarity of the molecules as a whole is high, form the smectic A_1 phase for short alkyl (alkoxy) chains and, additionally, the smectic A_d phase for long alkyl chains. The layer spacing rapidly expands when $n \geq 8$.

The smectics A_d belonging to group **b** are miscible with the smectics A_1 belonging to group **a** for members with long alkyl tails (subtype $S_{A_{1e}}$) and are immiscible with smectics A_1 of the same group for members with short alkyl tails. The smectics A_1 belonging to group **c** when mixed with the smectics A_1 with long alkyl tails belonging to group **a** or with the smectic A_d of group **b** dimerize and this causes the enhancement of the smectic region and also the creation of the nematic reentrant phase.

This work was supported by projects No. 205519101/p02 and No. 308159101 granted in the years 1991–1994 by the Committee of Scientific Research of Polish Governments

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