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S. Diele [a], G. Pelzl [a], A. Humke [a], S. Wünsch [a], W. Schäfer [a], H. Zaschke [a] & D. Demus [a]
[a] Sektion Chemie, Martin-Luther-Universität Halle-Wittenberg, Postfach, DDR-4010, Halle/S., German Democratic Republic
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New Binary Liquid Crystal Systems with the Phase Sequence S_A S_C S_A

S. DIELE, G. PELZL, A. HUMKE, S. WÜNSCH, W. SCHÄFER, H. ZASCHKE and D. DEMUS

Sektion Chemie, Martin-Luther-Universität Halle-Wittenberg, Postfach, DDR-4010 Halle/S. German Democratic Republic

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The phase diagrams of two binary liquid crystal systems are presented in which the phase sequence S_A S_C S_A occurs in a limited concentration range.

The structural differences of the high temperature S_A phase and the reentrant S_A phase are discussed on the basis of X-ray investigations.

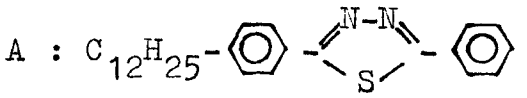
Keywords: smectic liquid crystals, binary systems, reentrant S_A phase, polymorphism, X-ray investigations

1. INTRODUCTION

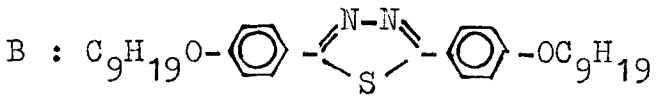
The reentrant nematic phases discovered in 1975 by Cladis[1] were intensively studied experimentally[2,3,4] as well as theoretically.[5,6,7] In most cases reentrant nematic phases were found in terminal-polar compounds and their mixtures. But recently also in binary systems of terminal-non polar compounds reentrant nematic phases were observed.[8–11] As shown in Reference 12 the reentrance of liquid crystalline phases is not restricted to nematic phases but was also found for a S_{Ad} phase of a terminal-polar compound. Recently in binary mixtures of terminal-non polar compounds the phase sequence S_A S_C S_A was detected.[13,14]

Now we present two binary systems of such behaviour, whereby in the second system a terminal-non polar compound is combined with a terminal-polar compound.

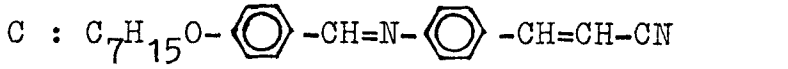
2. MATERIALS



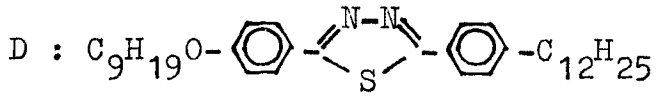
K 84 S_A 95 Is



K 97 S_C 192 Is[13]



K 81 S_A 170 N 191 Is[15]



K 74 S_C 169 Is

K : solid crystal
N : nematic
S_A,S_C: smectic A, smectic C
Is : isotropic liquid

The numbers between the phase symbols are the transition temperatures (°C).

The thiadiazole compounds A and D were prepared according to an instruction given in References 13 and 16

3. PHASE DIAGRAMS

The phase diagrams of the binary systems were studied by means of the contact method[17] and by determination of the transition temperatures of singular mixtures. The phase diagram of the system A/B (see Figure 1) is quite similar to that presented in Reference 13.

At middle concentrations an intermediate nematic phase appears although both single components do not possess nematic phases. As shown in Reference 18 such intermediate nematic phases originate from hypothetic nematic phases of the single components. The term "hypothetic" means that the nematic phase of the pure compound is thermodynamically unstable with respect to the smectic phases. This

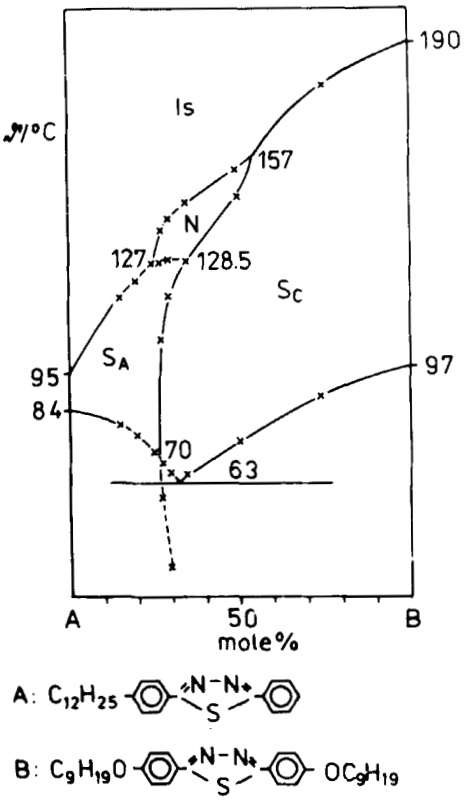


FIGURE 1 Isobaric phase diagram of the binary system A/B.

is indicated by the fact that lower homologues of the smectogenic thiadiazole compounds exhibit also nematic phases.[16]

The S_C phase exists in a wide concentration-temperature range. The transition curve $S_C \rightarrow S_A$ is nearly parallel to the temperature axis but the weak curvature at lower temperatures gives rise to the reentrance of the S_A phase below S_C in a limited concentration range between 70 and 72.5 mole-% A.

In the phase diagram of the system C/D in which the component C is a terminal-polar compound, the nematic phase of this compound is restricted to a small concentration region whereas the S_A phase is enhanced indicated by the extension over a large concentration-temperature range and by the maximum of the transition curve $S_A \rightarrow$ Is. Between 78 and 80 mole-% D the phase sequence S_A S_C S_A is found (without a nematic phase).

4. X-RAY INVESTIGATIONS

For the binary system C/D the thickness d of the smectic layers has been measured using a small angle X-ray equipment. The measurements were performed for mix-

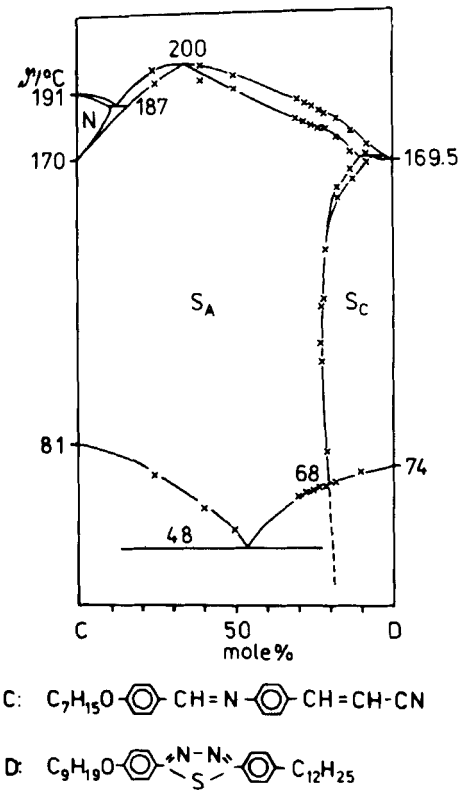


FIGURE 2 Isobaric phase diagram of the binary system C/D.

tures of several molar fractions (x_D = 0.2; 0.45; 0.6; 0.65; 0.72; 0.79; 0.87) including the pure compounds C and D. The *d*-values of each mixture have been measured as function of the temperature. The temperature dependence was not significant within the S_C and S_A phase region and its discussion can be omitted.

The dependence of the layer spacings on the concentration is shown in Figure 3. In this diagram three regions can be distinguished. In the first one, $0 \leqq x_D < \sim 0.5$ the layer spacings of the S_A phase (d^A) are greater than $\bar{L}$, calculated according to $\bar{L} = x_C L_C + x_D L_D$. A ratio $d/\bar{L} > 1$ often has been found in S_A phases of substances with a strong terminal-polar group and can be classified as S_{Ad} phase. In the S_{Ad} phases the smectic layers are assumed to consist of monomers as well as of dimers. This equilibrium is shifted more and more to the side of the monomers by incorporation of terminal-nonpolar molecules yielding decreasing differences $d - \bar{L}$ with increasing concentration of component D.

In the second region ($0.6 < x_D < 0.7$) the d^A values correspond to $\bar{L}$. This behaviour is proved in numerous binary systems which are constituted by substances with a classical rod-like molecular shape.[19]

In the third region ($0.7 < x_D < 0.9$) again a difference $d - \bar{L}$, but with negative sign, is observed. Such differences have been found in S_A phases of compounds

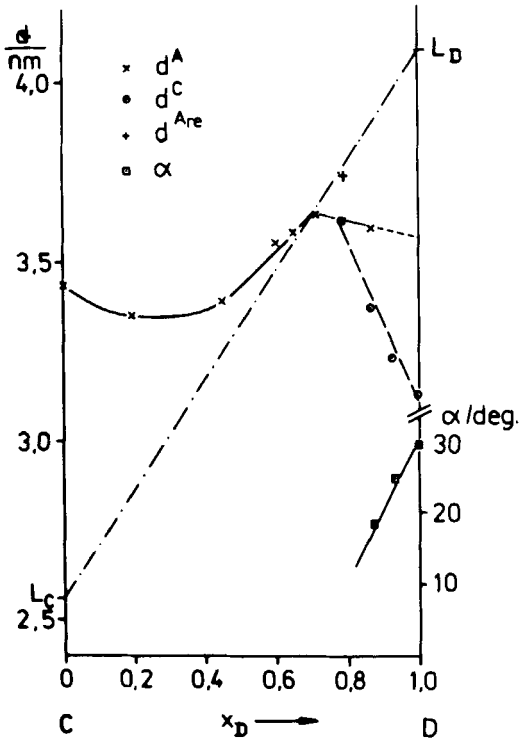


FIGURE 3 The dependence of the layer spacing d on the molar fraction for the binary system C/D. d^A, d^C, d^{Are} are the layer spacings of the S_A, S_C and S_{Arc} phase, L_C and L_D are the molecular lengths of the molecules C and D, respectively, in the most stretched conformation. The dotted line designates the averaged molecular length $\bar{L}$. The squares ⊡ on the right hand side of the Figure are the tilt angles α of the S_C phase.

with long alkyl chains. These differences have been explained by not fully stretched alkyl chains e.g. by deviations from their exact all-trans conformation. This influence is the greater the longer the chains are. Further on such behaviour has been observed in the neighbourhood of the S_A – N transition. The layer spacings of the S_C phases d^C are generally smaller than the averaged length of the molecules indicating a tilt angle of the long molecular axes with respect to the layer normal. In order to estimate the tilt angle according to the equation

$$\alpha = cos^{-1} d^C/d$$

we used d^A as denominator in the case of the mixture with $x_D = 0.87$ and extrapolated values (dashed line) for higher concentrations. These extrapolated values take into account the discussed chain shortening as a consequence of the trans-gauche transition. The estimated tilt angles are strongly dependent on the concentration. It tends to zero approaching the $S_C \rightarrow S_A$ transition line on the concentration scale. Therefore the tilt angle in the S_C phase of the mixture with $x_D = 0.79$ must

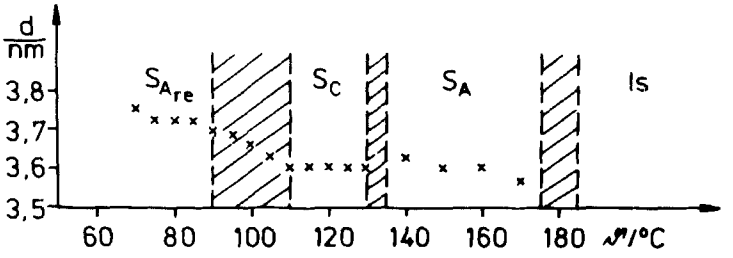


FIGURE 4 The layer spacing d as function of the temperature in the S_A, S_C and reentrant S_A phase (S_{Are}) of the binary mixture C/D (x_D = 0.79). The hatched regions indicates transition intervals.

be very low which explains that within the limits of error no difference between d^C and d^A has been observed (see Figure 4).

The d-value in the reentrant S_A phase is somewhat greater than the d^A values of the high temperature S_A phase and it does agree with $\bar{L}$. This result supposes the assumption that the alkyl chains of the molecules take on their full all-trans conformation in the reentrant S_A phase.

The results of the structural investigations agree with those of Sakashita *et al.*[20] obtained for a binary mixture of fluorenone derivatives which exhibit the phase sequence S_A S_C S_A in a relatively large concentration range. Sakashita *et al.* found that the layer spacing in the reentrant S_A phase is somewhat higher than that of the high temperature S_A phase. Similar to our results they observed only a very small difference of the d-values in the S_A and S_C phase. The tilt angle of the S_C phase which can be derived from their experimental data is very low. Contrary to our results the authors determined a ratio $d/\bar{L} > 1$ for the S_A phase as well as for the reentrant S_A phase ($d/\bar{L}$ = 1.018 in S_A and 1.025 in S_{Are}). From this the authors derived that the high temperature S_A phase possesses a monolayer structure whereas the reentrant S_A phase forms a partially bilayer structure although in both S_A phases $d/\bar{L}$ ratios have been found to be greater 1. Generally it seems to be problematically to postulate a partially bilayer structure if d/L is only a little bit greater than 1. The errors in the determination of the d-values and of the molecular length must be taken into consideration, e.g. using CPK molecular models to determine the molecule lengths a ratio $d/\bar{L} < 1$ can be obtained for the binary mixture of fluorenone derivatives.

The temperature dependence of the alkyl chain conformation is connected with energy effects, that means changes of the molar heat capacity. These temperature dependent changes may be responsible for the reentrant S_A S_C S_A phenomenon.

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