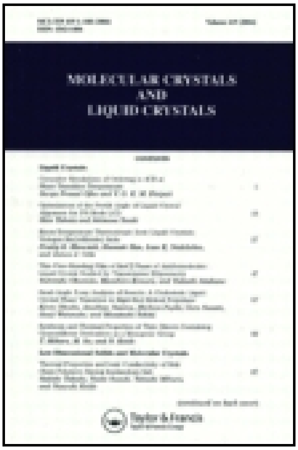

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Miscibility between the Smectic A Phase of A Conventional Liquid Crystal and the Lamellar Phase of an Inverse Salt

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MISCIBILITY BETWEEN THE SMECTIC A PHASE OF A CONVENTIONAL LIQUID CRYSTAL AND THE LAMELLAR PHASE OF AN INVERSE SALT

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Abstract The isobaric phase diagram of a binary system is presented which gives evidence that the smectic A phase of a conventional liquid crystal is completely miscible with the lamellar phase of an inverse salt. With respect to the rule of selective miscibility the latter therefore corresponds to the phase type smectic A. According to X-ray measurements in the salt component as well as in the mixtures the layer spacings d of the smectic A phase are clearly smaller than the molecular lengths resp. the average molecular lengths. A packing model is proposed for interpreting the experimental results.

1. INTRODUCTION

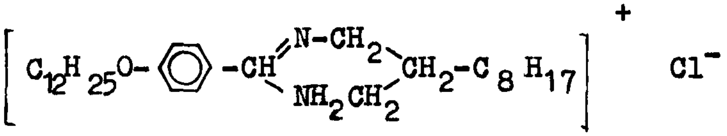
Up to now only a few classes of inverse salts are described in the literature which exhibit thermotropic smectic liquid crystalline phases[1-5]. According to optical observations the smectic phase of these salts is generally classified as a lamellar smectic A phase type. To our knowledge only the smectic phase corresponding to the phase of N-4-hexadecylpyridinium chloride was clearly identified as smectic A phase by X-ray investigations[6,7]. The layer spacing d of this S_A phase was found to be greater than the molecule length L. The ratio d/L varies between 1.1 and 1.3. In this paper the results of structural investigations for another class of thermotropic inverse salts are presented.

In addition, the miscibility of the lamellar phase of this inverse salt with the smectic A phase of a conventional liquid crystal is studied.

2. MATERIALS

We used for our investigations 5-n-octyl-2-[4-n-dodecylphenyl]-1,4,5,6-tetrahydropyrimidine-chloride(B) first synthesized by ZASCHKE[8].

B:



This substance has a transition scheme:

K 159 S 197 Is

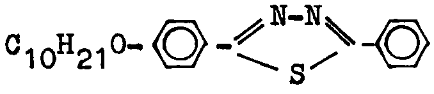
(K: solid crystal; S: smectic liquid crystal;

Is: isotropic liquid)

In microscopical observation the smectic phase of this substance exhibits a fan-shaped texture or a homeotropic texture which point at a lamellar phase corresponding to the A phase type.

As mixing component we used the following thiadiazole derivative:

A:



K 99 S_A 126 Is [9] (S_A: smectic A)

3. RESULTS

3.1. The Binary system

The isobaric phase diagram of the binary system is shown in Figure 1. The phase diagram was studied by polarizing microscopy using the contact method[10] and by determining transition temperatures in preparations of specific concentrations. The essential result is the complete miscibility between the lamellar phase of the inverse salt (component B) and the smectic A phase of a conventional liquid crystal (component A). A topological feature of the diagram is the minimum in the transition curve $S_A \longrightarrow Is$.

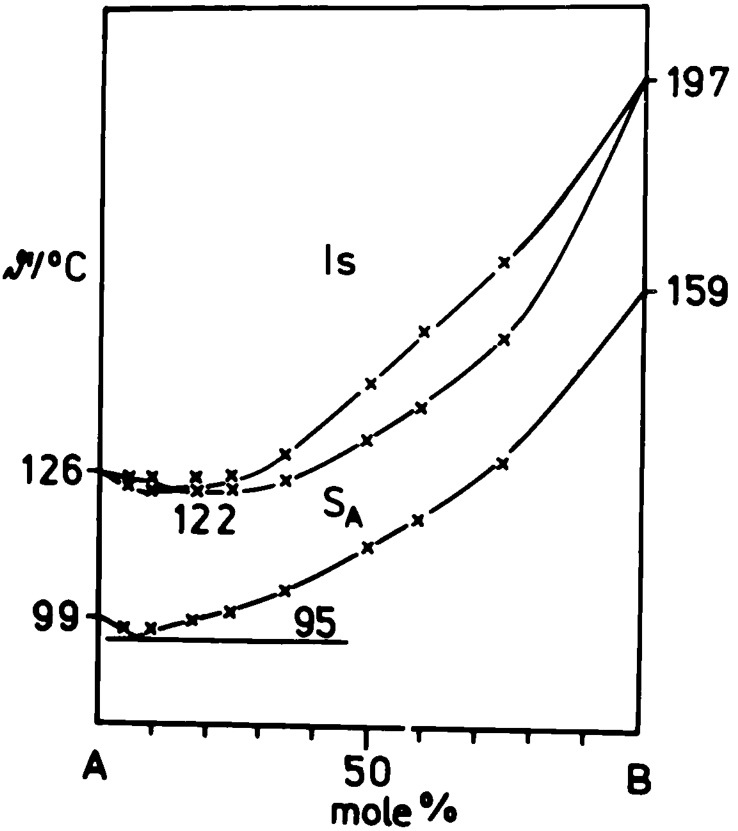


Figure 1 Isobaric phase diagram of the binary system A/B

3.2. X-ray Investigations

The layer spacings d of the smectic A phases were measured by X-ray diffraction using a small angle equipment. The smectic A phase of component A is a monolayer S_A phase where d is between 2.72 nm (126°C) and 2.76 nm (97°C). The molecular length is 2.78 nm. For the smectic A phase of the inverse salt (component B) the d-value was found to be 2.71 nm. This means that d is considerably smaller than the molecular length L of the most stretched conformation (L = 3.56 nm). In contrast to the smectic A phase of N-4-hexadecylpyridinium chloride[6] the ratio d/L is clearly smaller than unity (d/L = 0.76).

For the single components and for three mixtures of specific concentrations (75, 50, 25 mole-% A) the d-values of the S_A phase, the molecular lengths L resp. the average molecular lengths of the mixtures $\bar{L}$ are listed in Table 1. It is obvious from the Table that the ratio d/L decreases with increasing amount of the component B.

TABLE 1

mole-% A	d/nm^x	L/nm^{xx}	d/L
100	2.76	2.78	0.99
75	2.86	2.99	0.96
50	2.85	3.18	0.90
25	2.74	3.37	0.81
0	2.71	3.56	0.76

x) The layer spacing d shows a small temperature dependence. The values noted are related to a temperature just above the melting point.

xx) In binary mixtures an average molecule length $\bar{L}$ is taken which has been calculated by $\bar{L} = x_A L_A + x_B L_B$ where L_A, L_B are the molecular lengths of the compounds A and B and x_A, x_B are the corresponding molar fractions.

The results are illustrated in Figure 2 where the layer spacing d is plotted against the molar fraction. For comparison, the averaged molecular length is drawn. It is seen that at low concentrations of component B the layer spacing d increases and after that decreases to the value of the pure component B. Otherwise, the difference between L and d increases with increasing amount of component B.

It should be noted that in most cases the d-values of binary smectic A mixtures correspond nearly to the averaged molecule length $\bar{L}$ ($d/\bar{L} \approx 1$, see ref.[11]). Especially in terminal-polar compounds and their mixtures often $d/\bar{L} > 1$ was found [12,13,14]. Only a few smectic A materials are known where the ratio $d/\bar{L}$ is clearly smaller than unity [15,16].

To explain the essential difference between the molecular length and the periodicity of the smectic A layers a model for component B as sketched in Figure 3 is assumed. If the molecules are packed antiparallelly and shifted one to another in such a way that the positively charged pyrimidinium rings are neighboured to the oxygen atoms of the adjacent molecules, then a layer thickness in agreement with the experimental results can be modelled (Figure 3). An interdigitation of the molecules in the adjacent layers leads to a layer thickness considerably smaller than the lengths of the molecules. The relatively small alteration of

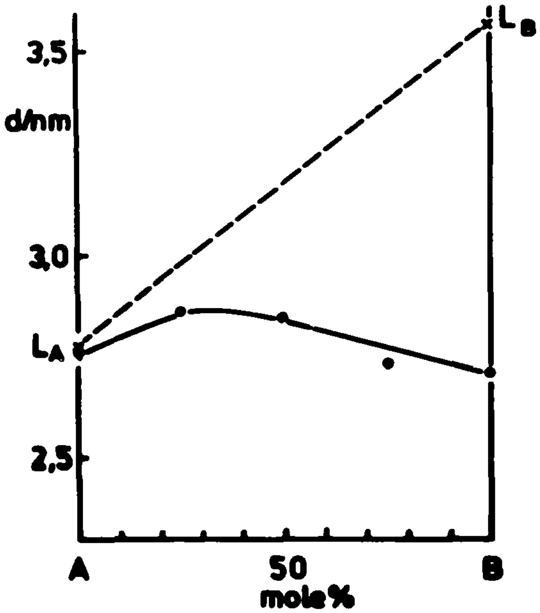


Fig. 2 . The dependence of the layer spacing d on the composition of the mixtures. The circles are the d-values of the smectic A-phase ; the dashed line corresponds to the average molecular length L

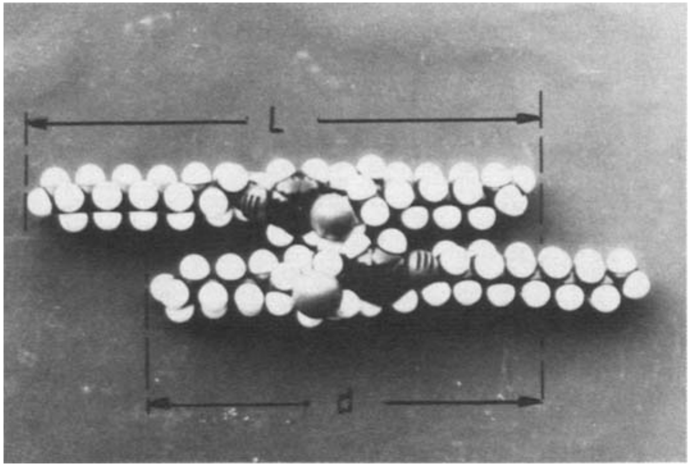


Fig. 3. Space filling model showing schematically the packing of the molecules of compound B in the smectic layers .

the layer thickness by incorporation of the molecules of the second component (A) points at a strong interaction between the molecules of component B.

It can be assumed that the chlorine is localized near to the positively charged centre of the pyrimidinium ring.

The specific conductivity of the lamellar phase of compound B was found to be between 10^{-3} and 10^{-4} Ohm^{-1} cm^{-1}. This value is in the same order of magnitude as for the lamellar phase of metal alkanoates [17,18] and for the isotropic melt of organic salts [19], but several orders of magnitude lower than for molten anorganic salts[19]. This result indicates the partial covalent bond character of compound B in the fluid phases which can explain the miscibility of the lamellar phase with smectic A phases of non-ionogenic compounds.

The complete miscibility with the S_A phase of a conventional liquid crystal proves that the lamellar phase belongs to the phase type smectic A. This is the first case of complete miscibility between a non-polar liquid crystal and a salt-like polar compound. Former investigations of the miscibility relations between non-polar and salt-like compounds led to the conclusion that complete miscibility is not possible since even in the isotropic state there is a distinct miscibility gap[20,21].

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