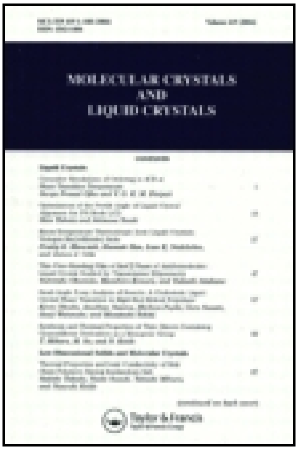

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

The Steric Influence on the Formation of Smectic Layers in Binary Systems

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Version of record first published: 22 Sep 2006.

To cite this article: S. Diele , G. Pelzl , A. Mádicke , D. Demus & W. Weissflog (1990): The Steric Influence on the Formation of Smectic Layers in Binary Systems, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 191:1, 37-47

To link to this article: http://dx.doi.org/10.1080/00268949008038577

Mol. Cryst. Liq. Cryst. 1990, Vol. 191, pp. 37–47
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Printed in the United States of America

The Steric Influence on the Formation of Smectic Layers in Binary Systems

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(Received September 15, 1989)

The layer spacings *d*, measured by an X-ray small angle equipment, have been used to characterize the smectic layers in binary systems. In mixtures consisting of conventional rod-like molecules the *d*-values show additive behaviour. By systematic modification of the molecular shape it can be evidenced, that in branched compounds the steric interaction causes a cage effect. In consequence of this the layer spacings do not behave longer additively and—under special conditions—induced S_A phases ("filled S_A phases") can be generated.

Keywords: Binary mixtures, X-ray investigations, steric interaction, filled phases, smectic, nematic, liquid crystals

1. INTRODUCTION

The wide spread miscibility between crystalline phases of the same designation leads inevitably to the question, in which kind the different molecules of the components of the binary mixtures are arranged in the mixed phases. Only a few investigations have been reported up to now as far as the discussion is restricted to substances without polar groups [[1] and further references given there].

The problem of the molecular packing is much more complicated, if one component of the mixture consists of branched molecules. The different cross section of the different parts of the branched molecules must lead to peculiarities of the packing in the mixed phase.

By a systematic modification of the substances used in the mixtures the importance of the steric interaction in the packing of the molecules is evidenced. The period of the density wave parallel to the layer normal, in short the *d*-values, measured by X-ray methods, shall be used for the discussion.

2. THE MIXTURES OF ROD-LIKE MOLECULES

The formation of smectic layers consisting of molecules of different length is the subject of a systematic investigation, published recently.[1] Only one example, which demonstrates the results with respect to the S_A phases shall be reported here. Figure 1 shows a binary system with components the molecular length of which are different by a factor of two. A complete miscibility of S_A phases has been proved.[2] Figure 2 displays the *d*-values as a function of the concentration, which can be described by a rule of additivity in the form of

$$d = x_A L_A + x_B L_B \tag{1}$$

in the greatest part of the system.
(x_A,x_B mole fractions; L_A,L_B lengths of the molecules in their most stretched form)

The small differences of the experimental values and the dashed line according to Equation (1) are within the limits of error. On the right side the *d*-values differ essentially from the straight line given by Equation (1). In the case of the pure component with very long aliphatic chains the well known result is explained by a deviation of the molecules from their most stretched form (or with other words by a higher gauche/trans ratio of the alkyl chains).

It is a remarkable result, found in further systems, too, that the difference between *L* and *d* decreases with increasing amount of the short component. It

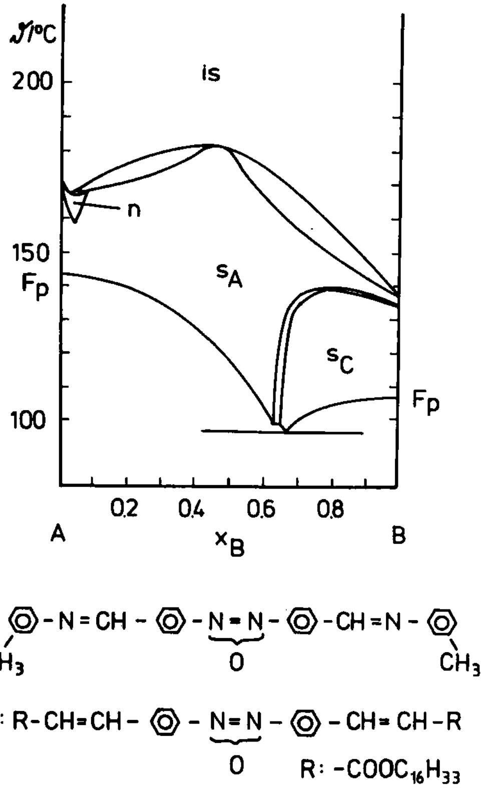

FIGURE 1 Phase diagram.

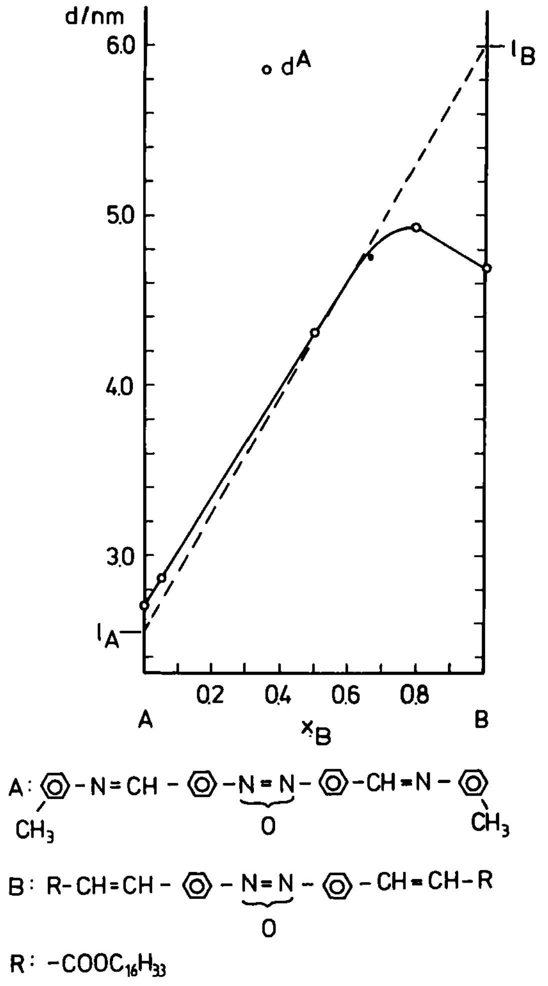

FIGURE 2 *d*-values of the system in Figure 1.

means that the long molecules tend to adopt their most stretched form in the binary mixture contrary to their behaviour in the pure state.

Based on the results obtained in numerous systems the following model (Figure 3) has been postulated:[1]

—The long and the short molecules are incorporated in one and the same layer.

—The short molecules are equally distributed around a mean plane.

—The long molecules, which adopt their most stretched form, penetrate into the neighbouring layers and push out in this way the mean plane leading to Equation (1).

—The process of incorporation of molecules with different lengths does not distort the long range order of the density period.

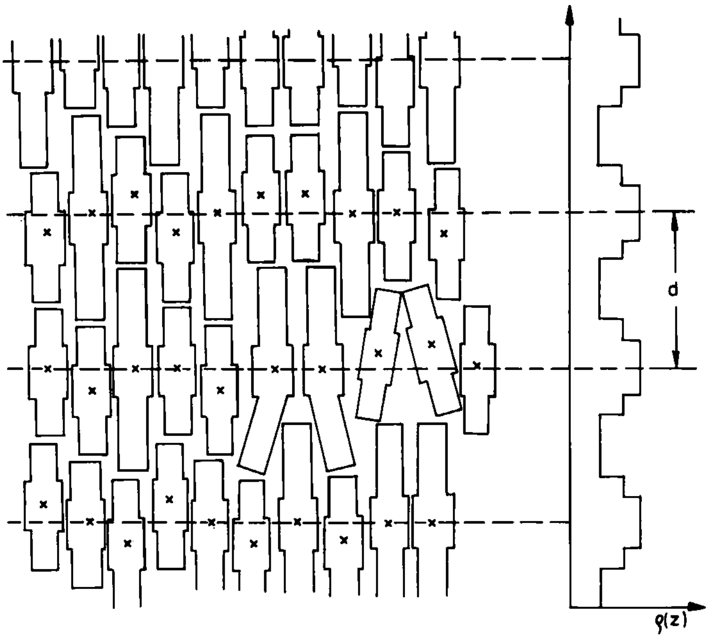

FIGURE 3 Proposed packing model.

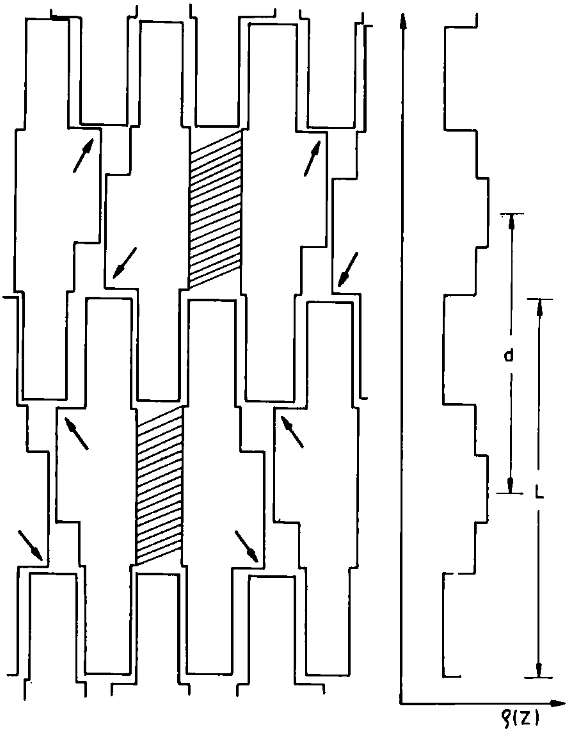

FIGURE 4 Proposed structure of laterally branched compound.

3. MIXTURES WITH LATERALLY SUBSTITUTED MOLECULES

The deviation from the rod-like form in molecules with lateral branches causes more difficulties in the formation of S_A phases. But the members of the series with the general formula[3]

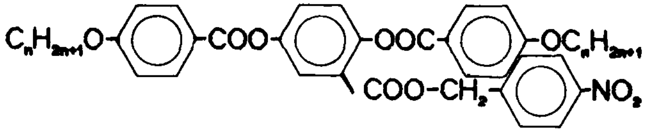

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exhibit stable S_A phases which have been proved by complete miscibility with conventional S_A phases and by X-ray investigations.[4,5] The creation of layers of S_A type by laterally branched molecules demands particular suppositions to get a dense packing within the layers. Figure 4 shows a proposed model which takes into account that the *d*-values have been found to be essentially smaller than the length of the molecules.[4] An interdigitation of the alkyl chains with the neighbouring layers has been assumed. But the interdigitation can fill out only partially the gaps which arise due to the different cross sections of the different parts of the molecule. The remaining gaps are hatched in Figure 4.

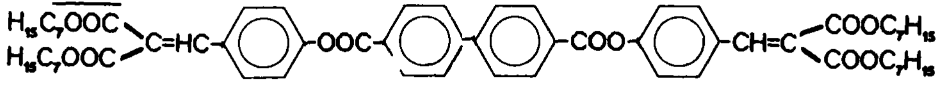
Contrary to other examples in Figure 5 a phase diagram is shown, in which the S_A phases are interrupted by a nematic region. In the system a second component has been admixed the molecular length of which is essentially smaller than the *d*-values of the S_A phase of the laterally branched compound. The *d*-values as a function of the concentration show a remarkable behaviour. In contrast to the results of section 2 the incorporation of the short molecules does not alter the *d*-values of the host structure in a wide concentration range. Obviously the short molecules fill out the gaps of the structure shown in Figure 4. The steric interaction causes a cage effect for the short molecules. The equal distribution around a mean plane is distorted and the *d*-values do not behave longer additively.

4. MIXTURES WITH BI-SWALLOW TAILED COMPOUNDS

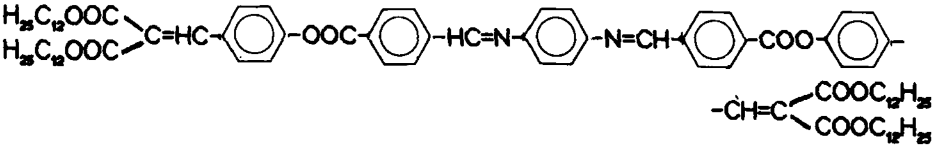
The steric interaction should be much more marked at compounds which are branched at both ends of the molecule. These pure compounds cannot form S_A phases, because the small waist in the middle part of the molecules would lead to gaps destabilizing the S_A layers. Only nematic or monotropic S_c phases have been found. However, by admixing a second component it should be possible to fill out the gaps[6] and to allow the existence of S_A phases.

For miscibility studies we used the following bi-swallow tailed compounds:

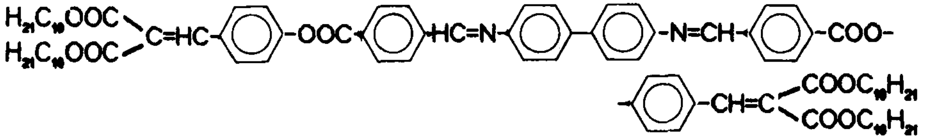
4DS7 /7/



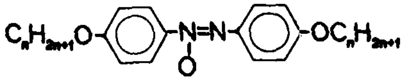
5DS12 /8/



6DS10 /8/



These substances have been mixed with conventional compounds of the general formula:



with n = 1 (C1), n = 5 (C5), n = 18 (C18)

In the first three examples one and the same bi-swallow tailed compound (4DS7) is mixed with substances of different molecular length (Figures 7, 8, 9). In all cases the pure components exhibit only stable nematic phases. But in concentration regions around sixty or seventy mole percent induced S_A phases appear. Because this phase is caused by filling out the gaps it has been called "filled S_A phase."[6] In Figure 10 the structural data of the three binary systems are compiled. The length of the middle part of the bi-swallow tailed compound is 2.65 mm. The d-values of the S_A phases, which are nearly independent of the temperature, are compared at the mole fraction x_B = 0.6. As far as the length of the second component is shorter (C1) or comparable (C5) to the length of the gaps the d-values are greater than the averaged molecular length which would be expected according to Equation (1). In the third example, in which the length of the second compound (C18) is essentially greater, the measured d-value is smaller than the value according the Equation (1). Here the structure can be explained similar to the structure discussed in section 2.

The result, that the d-values of the mixtures with C1 and C5 nearly agree, supports strongly the influence of the host structure. The steric interaction leads to a cage effect in the consequence of which an induced S_A phase appears.

Finally it should be pointed out that the d-values are altered in the mixtures in which the second component (C1) is always the same and the bi-swallow tailed

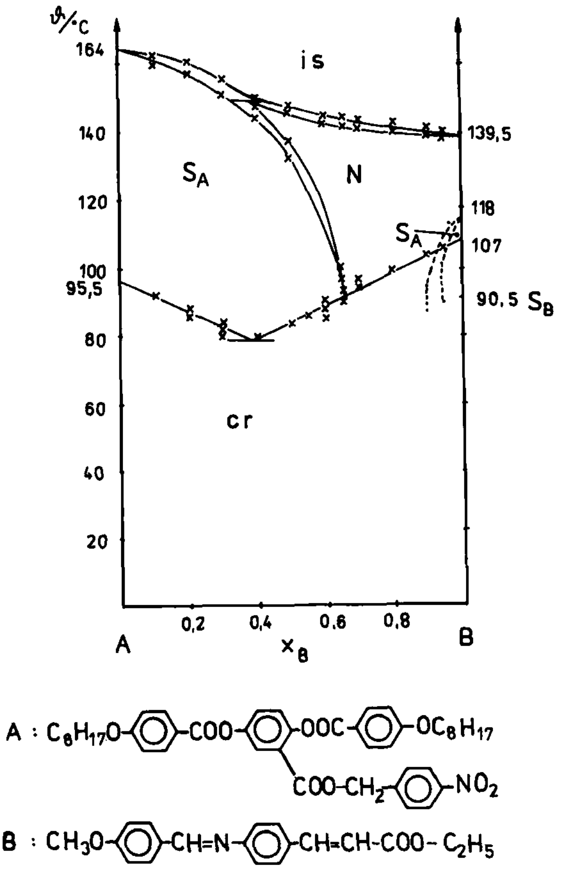


FIGURE 5 Phase diagram.

compound is changed. In the sequence 4DS7, 5DS12 and 6DS10 the length of the middle part is elongated. In the last case it is more than twice of the length of compound C1. That means—according to our model—that there is more space for an incorporation of the short molecules. Consequencely the ratios $d/\overline{L}$ increase in this sequence and although the total lengths of the molecules of 5DS12 and 6DS10 agree, the corresponding d-values of the mixtures are different (Figure 11).

5. SUMMARY

By a systematic modification of the molecular shape of the mixing components the influence of the steric interaction on the packing in S_A phases has been studied. The d-values have been measured as a function of the concentration.

As far as components with a conventional rod-like shape were mixed the lattice

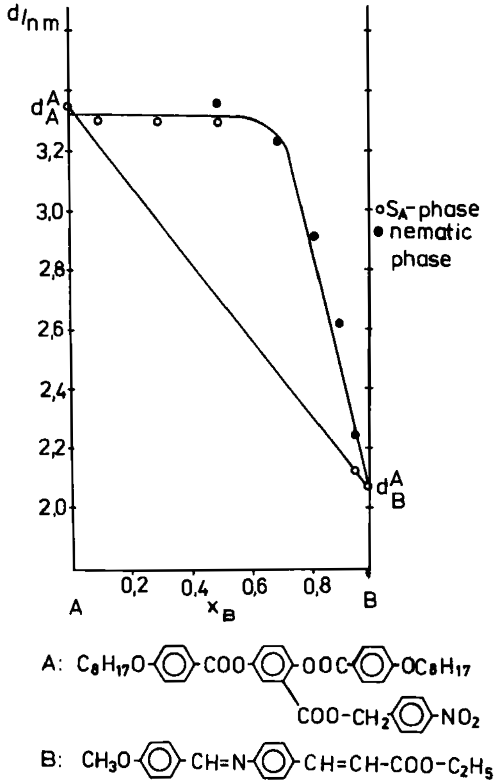


FIGURE 6 *d*-values of the system in Figure 5.

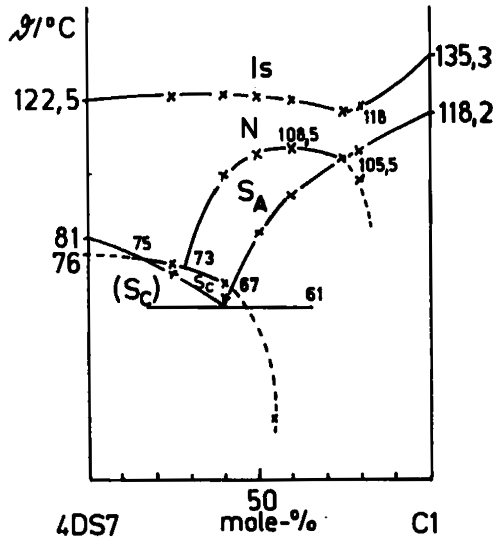


FIGURE 7 Phase diagram.

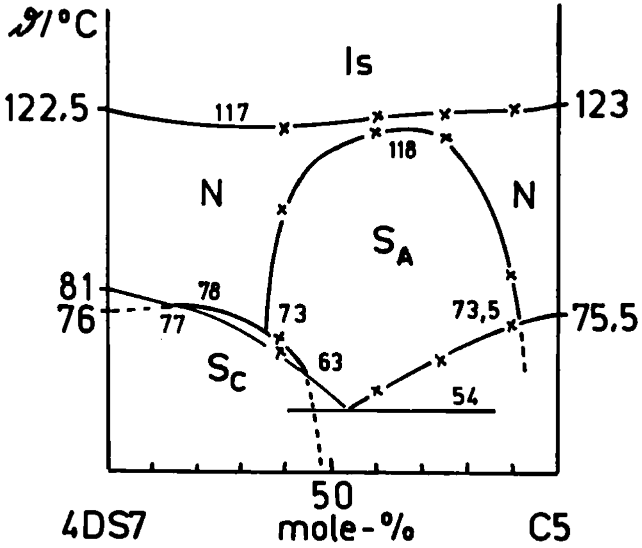


FIGURE 8 Phase diagram.

parameters behave additively. This dependence is changed if one component exhibits a branched shape which results in cavities of the host structure. The steric interaction now leads to a cage effect and the *d*-values are determined mainly by the host molecules. In the case of the filled phases the steric interaction yields an induction of S_A phases.

In such cases the ratio $d/\overline{L}$ is found between 1.1 and 2.13. With respect to these results the classification of S_A phases in non-polar systems into S_{Ad} or S_{A2} seems to be doubtful and should be avoided.

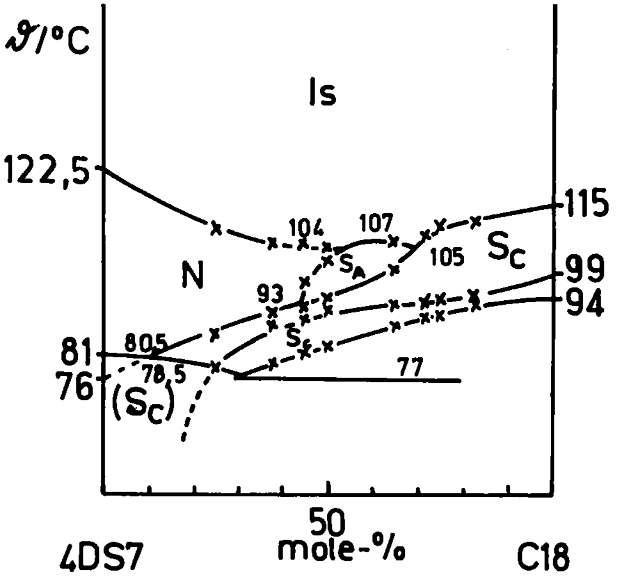


FIGURE 9 Phase diagram.

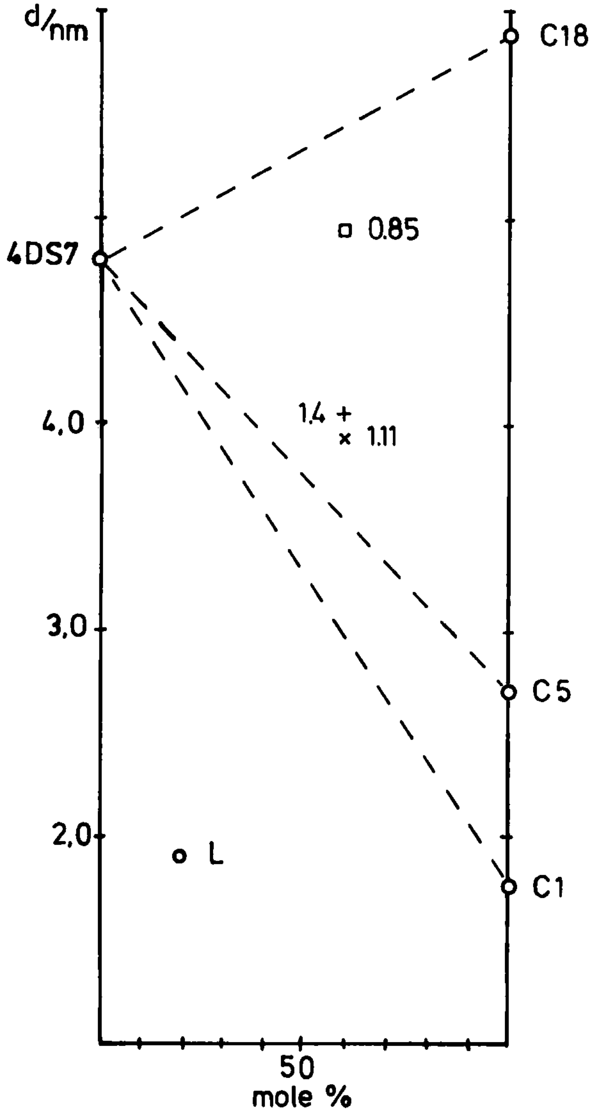


FIGURE 10 *d*-values obtained in the phase diagrams.
4DS7/C1 ×
4DS7/C5 +
4DS7/C18 □
The numbers mean the ratios $d/\overline{L}$ of the corresponding mixtures.

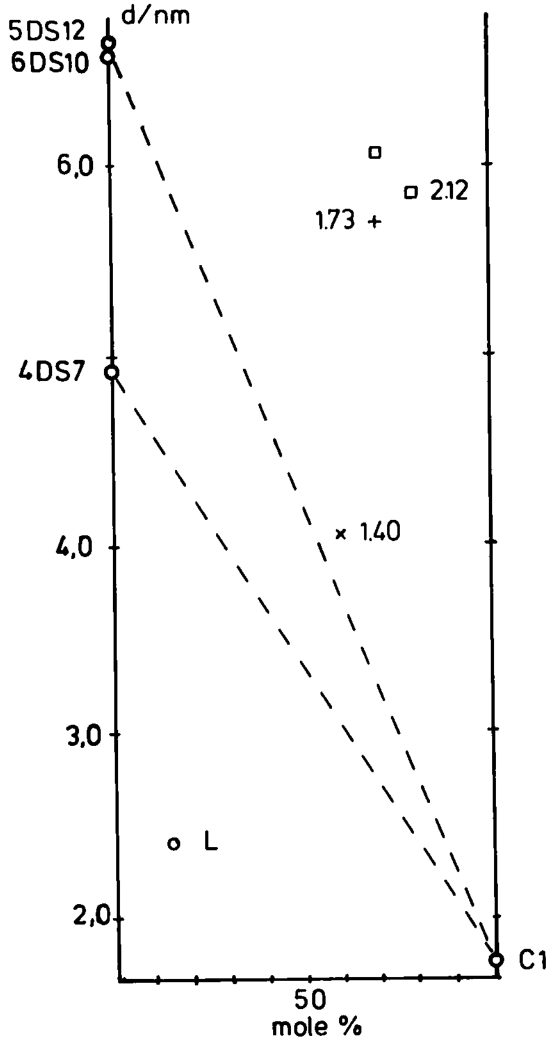


FIGURE 11 *d*-values obtained in the phase diagrams
4DS7/C1 ×
5DS12/C1 +
6DS10/C1 □
The numbers mean the ratios $d/\bar{L}$ of the corresponding mixtures.

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