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New Topology for A N_{re} - S_A - S_C Multicritical Point

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NEW TOPOLOGY FOR A N_{re} - S_A - S_C MULTICRITICAL POINT

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Another example of N_{re} S_A S_C multicritical point is evidenced here with a new topology in a (x,T) binary diagram. In particular a second order N_{re} - S_C line is confirmed and the tilt angle seems to be a pertinent orientational order parameter for this nematic-smectic change.

INTRODUCTION

Recently a reentrant nematic - smectic A - smectic C multicritical point has been described [1]. This inverted N A C point was observed in a binary (x,T) isobaric diagram (1 atm) between two long cyano compounds [2]. The most remarkable feature is the second order character for the three transition lines N_{re} - S_A, S_A - S_C, N_{re} - S_C. R. Shashidhar et al. [3] also found a N_{re} - S_A - S_C point with a similar topology in the (P,T) diagram of a pure cyano derivative but the N_{re} - S_A transition is claimed first order.

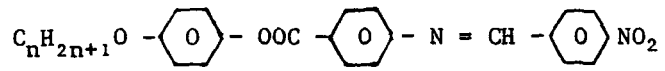
At any rate these new facts give support to the fundamental concept concerning the N A C multicritical points which are not triple points from three lines of first order transitions [4].

New polymorphisms in which the S_C phase occurs below the reentrant nematic give opportunities for other N A C points for which it is necessary to specify whether they are common triple points or multicritical points. For example in the binary system of non polar headed compounds studied by S. Diele et al.[5], the topology of the N_{re} - S_A - S_C point seems to agree with the general idea of a nematic-smectic

line joined by the S_A - S_C line. Unfortunately no thermodynamical data is available around this point. Another example of a N_{re} S_A S_C point with a low temperature S_C phase was recently reported [6]. This latter point is clearly revealed here as the intersection of three second order lines. However the topology shows that the nematic to smectic line cannot be continuous across this N_{re} S_A S_C multicritical point.

RESULTS

Mixing two homologues (C_{10}, C_{11}) of a three rings nitro series recently synthetized [7]:



$$C_nH_{2n+1}O - \langle O \rangle - OOC - \langle O \rangle - N = CH - \langle O \rangle NO_2 \qquad (1)$$

we accurately studied the temperature - molar fraction phase diagram (Fig. 1) by means of microscopic observations and D.S.C. measurements.

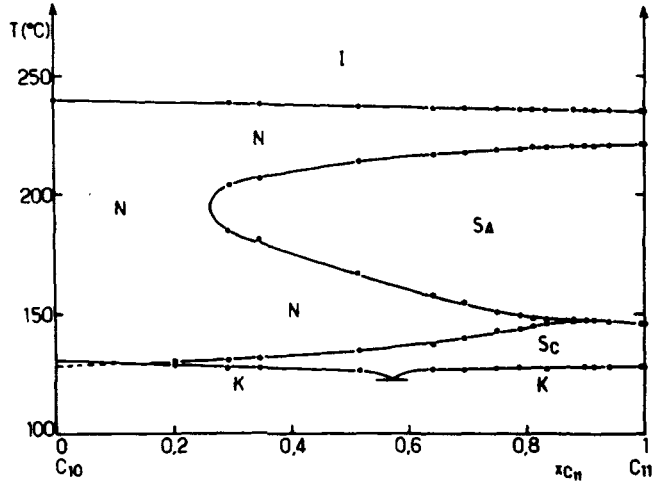


Figure 1 : Binary isobaric diagram (1 atm) between n = 10 (on left) and n = 11 (on right) compounds of the series (1)

Let us note that the three lines of phase transitions $S_A - S_C$, $S_A - N_{re}$, $N_{re} - S_C$ are enantiotropic around the N_{re} AC point. In contrast with the earlier N_{re} AC multicritical point at P = 1 atm.[1] we can undoubtly see (Fig. 2) that the N_{re} S_C line is not the extension of the N_{re} S_A line through the intersection point. In addition we confirm that this point is a multicritical one since the meeting of three second order transition lines. Indeed no D.S.C. peak is revealed running the maximum accuracy of the Dupont 990.

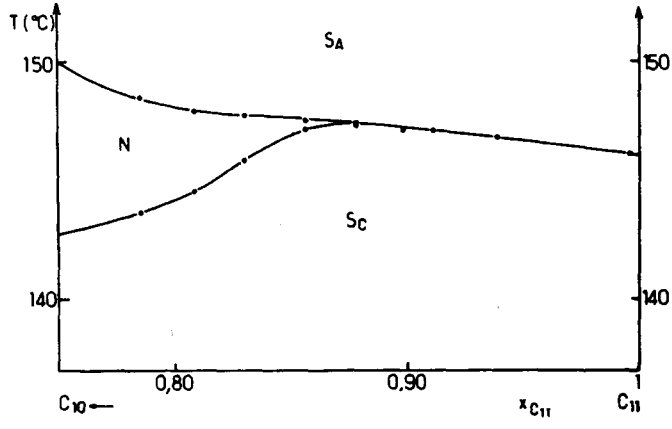


Figure 2 : Detail of the diagram near the N_{re} AC point.

Taking into account the thermodynamic stability of the different mesophases, we performed X-Ray experiments in order to specify the layering order in this nitro system :

As for most polar rods with terminal cyano or nitro group we find in the high temperature S_A phase of the C_{11} that the layer spacing d is somewhat larger than the molecular length ℓ in its extended conformation (SASM model) ($\frac{d}{\ell} \simeq 1,1 - 1,2$). This layer spacing decreases as the temperature decreases and at the $S_A - S_C$ phase transition the ratio $\frac{d}{\ell}$ is close to 1 (Fig. 3).

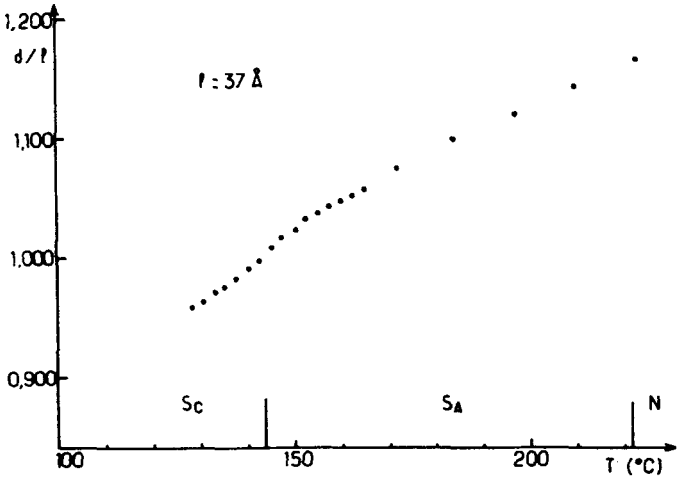


Figure 3 : Smectic layer thickness as function of temperature (Guinier camera - powder sample) ; n = 11 compound.

Thus, a partial bilayer S_C is not clearly evidenced here, in contrast with other polar systems [8,9].

In addition, considering now two mixtures along the C_{10}- C_{11} diagram which respectively exhibit $N - S_C$ ($x_{C_{11}} = 0.09$) and $N_{re} - S_C$ ($x_{C_{11}} = 0.75$)transition, this critical ratio $\frac{d}{\ell} \simeq 1$ seems to be directly connected to the occurence of the tilted phase (Fig. 4).

From the X-Ray analysis with an orientated sample of the $x_{C_{11}} = 0.76$ mixture a weak tilt angle ($\sim 10°$) is estimated in the S_C phase a few degrees below the reentrant nematic. In the same way no "skewed cybotactic groups" are observed in the reentrant phase [10]. As it is the case for the $S_A - S_C$ transition (Fig. 3), these results strongly suggest that the tilt angle is a pertinent orientational order parameter for the $N_{re} - S_C$ transition at least in the vicinity of the N_{re} AC point.

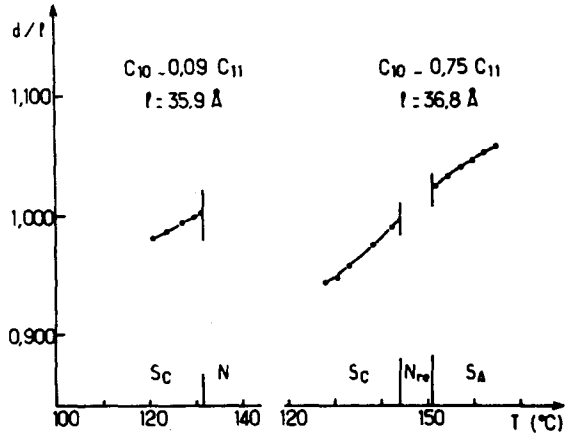


Figure 4 : Smectic layer thickness as function of temperature (Guinier camera - powder sample) for two mixture $x_{C_{11}}$ = 0.09 and $x_{C_{11}}$ = 0.76.

With $\ell = x_{C_{10}} \ell_{C_{10}} + x_{C_{11}} \ell_{C_{11}}$

The $d > \ell$ values in S_A phase give evidence for an antiparallel dipolar arrangement of the molecules but only one layering period is observed throughout the $S_A - N_{re} - S_C$ sequence. Even though generally with the three rings polar compounds the intermediate reentrant nematic between two smectic phases exhibit two types of smectic fluctuations [11]. In this nitro system the low temperature smectic C phase does not originate from a second modulation mode [12] and could explain such a behavior.

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