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Critical or tricritical S_{Ad} - S_{A2} point in a (temperature-molecular length) phase diagram ?

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Résumé. — A partir d'observations microscopiques, d'analyses enthalpiques différentielles et de mesures de rayons X, nous avons étudié la transition Smectique A_d -Smectique A_2 de sept composés de la série des 4-n alcoxyphenyl-4' cyanobenzoyloxy benzoates (DB_nO). Nous montrons en particulier l'influence de la plage de température d'existence de la phase S_{Ad} sur l'enthalpie de transition. L'ensemble des résultats suggère un comportement critique ou tricritique dans un espace thermodynamique température-longueur moléculaire.

Abstract. — From microscopic observations, DSC experiments and X-ray data the Smectic A_d -Smectic A_2 transition is studied in seven compounds of the 4-n alkoxy phenyl-4' cyanobenzoyloxy benzoate series (DB_nO). In particular the excess enthalpy associated with this transition is found to depend on the width of the S_{Ad} range. These results suggest either tricritical or critical behaviour in a (T , molecular length) phase diagram.

1. Introduction.

Several kinds of smectic A phases differing in the magnitude of the layer spacing d relative to the molecular length l have been found [1]. In the S_{Ad} , $1 < d/l < 2$, whereas this ratio is nearly equal to 2 in S_{A2} .

The first S_{Ad} - S_{A2} phase transition was observed in a pure *long core* cyano derivative, the 4-n-heptyl phenyl-4'-cyanobenzoyloxy benzoate (DB_7 for short) [2]. The formula of this compound is as follows :

This polymorphism was ascertained in the homologues of the DB_7 with longer alkyl chains (DB_n) [1, 3] or alkoxy chains (DB_nO) [1, 3] and revealed in various other series [4, 5].

Referring to the earlier X-ray characterization [1, 2, 4, 5] of this transition we recall that a diffuse scattering in S_{Ad} appears to be sharpened around $2\pi/l$ at the S_{Ad} - S_{A2} transformation. However, the surimposition of the 002 bilayer Bragg reflexion sometimes complicate the analysis.

Our purpose here is to specify the thermodynamic evolution of this kind of S_A - S_A transition as a function of the length of the aliphatic chain varying this parameter over a large extent in the DB_nO series :

2. Experimental.

The DB_nO compounds of this study were synthesized in our chemistry laboratory. In figure 1 the transition temperatures are plotted against n , number of carbons in the chain, relative to the isotropic, nematic, S_{A_d} and S_{A_2} phases. We note that the S_{A_d} phase becomes visible for $n > 6$ and it exists within a larger and larger temperature interval as n increases. These transition temperatures are obtained from microscopic observations between glass slide and cover slip. In contrast with earlier investigations of DB_7 compound [2], at the transformation S_{A_2} to S_{A_d} , a textural change is detected in a planar part of the preparation as a sudden multiplication of the focal conics (Fig. 2a). Although these reversible modifications are weaker and smoother for the higher homologues, they are still observable within a 2 K variation (Fig. 2b).

Note that textural modifications at the S_{A_d} - S_{A_2} transition have been also evidenced for other compounds [6, 7].

The DSC traces in figure 3 were carried out by means of a DUPONT 990 apparatus with the same high sensitivity recording ($0.005 \text{ mcal s}^{-1} \text{ in}^{-1}$), the same cooling rate (2° min^{-1}) and the same sample weight (7 mg) for all the compounds ($n = 7$ to 13). We note that the excess of enthalpy decreases rapidly with increasing n . Ultimately, neither discontinuous changes in enthalpy nor continuous variations are detectable for $n = 13$.

For the $n = 7$ and 8 compounds the excess of enthalpy is rather large (400 and 250 mcal g^{-1}) and could include a latent heat to the pretransitional increase of the specific heat. In contrast with these two cases, the resolution of the DSC recordings rules out the existence of a latent heat contribution for the higher homologues (Figs. 3 and 4).

Fig. 1. — Transition temperatures *versus* aliphatic chain length for the DB_nO series.

Fig. 2. — The focal conic textures of the S_{A_2} and S_{A_d} phases ($\times 400$), (a) for $n = 8$: Smectic A_2 phase (on the left) $T = 178\text{ }^{\circ}\text{C}$, Smectic A_d phase (on the right) $T = 180\text{ }^{\circ}\text{C}$; (b) for $n = 12$: Smectic A_2 phase (on the left) $T = 168\text{ }^{\circ}\text{C}$, Smectic A_d phase (on the right) $T = 170\text{ }^{\circ}\text{C}$.

These observations compare well with the results from small angle X-ray scattering on powder samples which yield the temperature variation of the d/l ratio, where d is the layer spacing and l the molecular length, in the most extended conformation (SASM model) (Fig. 5).

In particular, the evolution of this parameter is quite smooth for $n \geq 11$ and contrary to the lower homologues, we cannot locate a S_{A_d} - S_{A_2} change by this technique.

3. Discussion.

In our calorimetric measurements the sharp enthalpy increase at the transition for the $n = 7$ compound could be interpreted as a proof of a first-order character, although the DSC method cannot really distinguish a discontinuous change in enthalpy from a rapid but continuous variation. However it should be stressed that, increasing the aliphatic chain, our results do not correspond to a decrease in the latent heat but rather to a decrease in the entropy variation due to the fluctuations.

Thus if we assume that part of the excess of enthalpy for DB_7O does correspond to a latent heat, we suggest two possible meanings for our experimental results when we extend them to a temperature-molecular length space :

- either there exists a tricritical point along the S_{A_d} - S_{A_2} line : this supposes that there is a hidden symmetry between S_{A_d} and S_{A_2} [8],
- or the S_{A_d} - S_{A_2} line ends somewhere at a critical point. The vicinity of such a point could induce, for the homologues with long chains, noticeable fluctuations of the specific heat yet without phase transition. Nevertheless, beyond this point, the sudden change for the focal-conics should depend on kinetic effects which have not been observed. This second hypothesis implies a S_{A_d} - S_{A_2} transition without any symmetry change, as theoretically predicted by P. Barois *et al.* [9]. This situation is also qualitatively described from a microscopic model considering the thermal evolution of a degree of head to head association of dimers [10].

Fig. 3. — DSC cooling curves for the DB_nO series in the Smectic A region (same weight : $m = 7$ mg).

None of our low resolution techniques allow us to locate this critical (or tricritical) point for a system (pure compound or binary mixture) beyond $n = 7$.

As a matter of fact, high resolution experiments are clearly needed to resolve the questions of the localization and of the nature of this point.

Finally we remark that evidence is given for a strong connection between the width of the thermal range of the high temperature phase S_{A_1} and the thermodynamical behaviour of the transition. If this evolution is confirmed in other homologous series it has to be compared with what exists for the N - S_A transition taking into account low resolution works [11] as well as recent high resolution results [12, 13].

Fig. 4. — Comparative DSC recordings for the $S_{A_d}-S_{A_2}$ transition in the compounds $n = 7, 8, 9$ ($m = 7 \text{ mg}$).

Fig. 5. — Thermal variations of the reduced layer thickness for the DB_nO series, using Guinier camera (Hübert) and CoK_{α_1} monochromatic radiation.

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