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## Incompatibility of the constituent parts of smectogenic molecules

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**Résumé.** — On a considéré le produit smectogène : 4-acétyl-4'-*n*-tétradécyloxyazobenzène. On a déterminé le diagramme de phases du système binaire composé de ses deux parties constitutives, à savoir le dodécane et le 4-acétyl-4'-*n*-acétyloxyazobenzène. Une lacune de miscibilité a été observée à l'état liquide et interprétée comme argument en faveur de l'importance du rôle joué par le caractère amphiphilique dans l'apparition des mésophases smectiques.

**Abstract.** — The smectogenic compound 4-acetyl-4'-*n*-tetradecanoyloxyazobenzene was considered. The phase diagram of the binary mixture of its constituent parts, that is dodecane and 4-acetyl-4'-*n*-acetyloxyazobenzene, was determined. A miscibility gap in the liquid state was observed. This was considered as support for the view that the amphiphilic nature of the molecule plays an important role in the formation of the smectic mesophase.

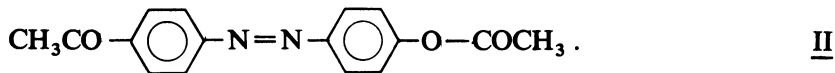
A few years ago, it was suggested that smectic mesomorphism was related to the amphiphilic character of the smectogenic molecules [1]. Indeed, smectogens are formed of two elongated parts, which are usually a needle-like aromatic core and one or two flexible aliphatic chains, which are different in chemical nature and, hence, incompatible with one another to some extent. In the smectic state, the two parts of the molecules would segregate [2] : the polar moieties and the paraffin chains would locate themselves in distinct sublayers [3], alternately and periodically piled up in space. In this way, the polar cores would have neighbouring polar cores in sufficient lateral proximity so as to easily satisfy their specific interactions. Some of the investigators in the field of liquid crystals [4] understand the smectic layering as going so far as to imply the creation of reasonably sharp interfaces between the aromatic and the aliphatic sublayers; others [5] prefer to consider that, instead, the layering is independent of the location of the aliphatic chains with respect to the aromatic cores.

To check for the internal incompatibility of the smectogenic molecules and for the importance of their amphiphilic character, we decided to determine the phase diagram of binary mixtures of their constituent parts, i.e. of linear paraffins with elongated, rigid, aromatic molecules. In

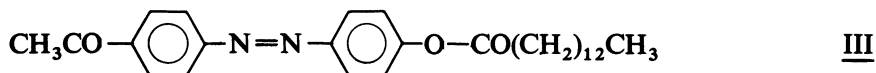
this preliminary work, we restricted ourselves to considering the case of binary mixtures of *n*-dodecane :



with 4-acetyl-4'-*n*-acetoxyloxyazobenzene :



Both products pass directly from the crystalline into the isotropic liquid state, at temperatures of  $-12^\circ\text{C}$  and  $+130^\circ\text{C}$ , respectively. It is worth noting that 4-acetyl-4'-*n*-tetradecanoyloxyazobenzene :



which results from the combination of I and II within a single molecule, exhibits a smectic A mesophase in the temperature range of  $107$  to  $118^\circ\text{C}$  [6]. Observations of phase separation were performed visually, using an experimental set-up described previously [7]. Mixtures of I and II were heated until they reached the homogeneous isotropic liquid phase, then carefully cooled down until sudden turbidity and, ultimately, macroscopic phase separation could be observed.

Figure 1 illustrates the experimental data that we obtained. Clearly, there is a miscibility gap in the liquid state, the two components not being miscible in all proportions. The two-phase region corresponding to the coexistence of two liquid solutions — one rich in I, the other in II — is quite extended in composition as well as in temperature. The critical solubility point is located at  $166.7^\circ\text{C}$  for a molar concentration in dodecane of 0.60 (i.e., 47.5% in weight). When taken as pure independent chemical species, the two moieties of the particular smectogenic substance III considered in this work are, therefore, incompatible within a large temperature range.

The critical temperature found is well above the melting temperatures of the two pure components. It is also well above the clearing point of compound III, i.e., the smectic A/isotropic transition temperature. This phenomenon is easy to understand, for it simply comes from entropic reasons. In order for I and II to segregate under given temperature conditions, their repulsive interaction coefficient (Flory's  $\chi$  parameter) must be much stronger if they were bound together

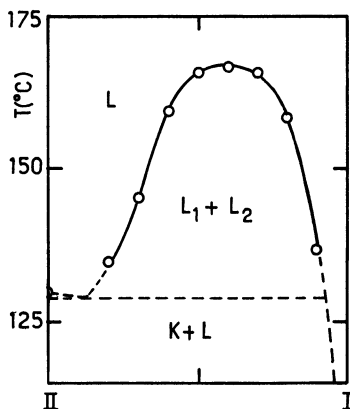


Fig. 1. — Binary phase diagram of I/II : temperature as a function of molar concentration (L,  $L_1$  and  $L_2$  : liquid phases ; K : crystal).

within a single molecule III, than if they were free and independent. A similar situation has been observed in the case of polymers, where it was theoretically predicted [8] that the clearing point of block copolymers would be substantially lower than the critical solubility temperature of the corresponding homopolymers.

Also, upon considering the thermal behaviour of homologous smectogenic series [6, 9, 10], one finds that the transition temperatures from the smectic to the nematic or to the isotropic liquid phase pass through a maximum value as a function of the number  $n$  of carbon atoms in the aliphatic chains of the molecules. This effect is obviously another manifestation of the amphiphilic character of smectogenic substances and of their intramolecular incompatibility. It can indeed be shown that, for a given smectogenic system, i.e., for a given repulsive intramolecular interaction parameter, the temperature at which the aromatic stems and the aliphatic chains can mix up « homogeneously » (as they do in the nematic or the isotropic liquid phase, the cybotactic [11] fluctuations not taken into account) must not depend merely upon the length of the aliphatic chains, but must actually go through a maximum value, since the product  $\chi n(\chi \sim T^{-1})$  goes through a minimum value as a function of chemical composition  $f$  ( $f \sim n/(n + a)$ ) [8].

Following the preliminary experimental data reported in this letter, further studies of binary mixtures are presently in progress. Two points are at the moment being investigated : the rôle of the length and the chemical nature of the flexible component, and the importance of composition fluctuations around the critical solubility point in the homogeneous liquid.

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- [2] Because of the covalent bond linking the two constituent parts of the molecules, segregation proceeds only on a local scale (an amphiphilic molecule being something more than simply the sum of its parts). From a general standpoint, it is clear that only miscibility leads to a positive statement, at least as far as symmetry is concerned : in the case of a miscibility gap, the two coexisting phases are, strictly speaking, not qualitatively but just quantitatively different. In the smectic state, the local internal segregation of the molecules does by no means correspond to a macroscopic two-phase separation ; it implies the preferential location of the two moieties within distinct sublayers, with the possibility of diffusing across the interfaces.
- [3] The layer-like morphology of the segregation microdomains in smectics is probably related to the rather rigid and elongated form of the molecules, on the one hand, and to the existence of rather sharp interfaces between the polar and the aliphatic moieties, on the other. Indeed, cylindrical or spherical microdomains, similar to those observed in soap solutions, are strongly disadvantaged with respect to the layer-like microdomains, due to the high energy price paid for arranging rigid rods in a splay configuration, while keeping the interfaces sharp.
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- [11] Cybotactic fluctuations are indicative (see DE GENNES, P. G., in *The Physics of Liquid Crystals* (Clarendon Press, Oxford) 1974), of local layering and of local segregation of the molecules. These fluctuations should also exist in the nematic or the isotropic state for substances whose aliphatic chains are not sufficiently long to give rise to smectic phases. Now, the question arises of whether the cybotactic fluctuations could not profitably be compared with the micellar fluctuations observed with soap-like materials. It should then be of interest to study the cybotactic fluctuations as a function of concentration and temperature in the hope of finding a critical concentration and/or temperature beyond which they rapidly disappear.

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