Generalization of the polymorphism with 2D fluid smectic phases

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Generalization of the polymorphism with 2D fluid smectic phases

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Résumé. — A partir d'observations microscopiques sur gouttes libres nous avons localisé différentes lignes de transition entre phases smectiques fluides bidimensionnelles dans des diagrammes binaires concentration-température. Nous avons en particulier défini un critère de changement de texture pour identifier la transition $S_{\tilde{C}}$-$S_{\tilde{A}}$. Nous concluons à l'ordre de succession des phases $S_{\tilde{C}}$-$S_{\tilde{A}}$-$S_{A_{cre}}$ par abaissement de la température.

Abstract. — On the basis of microscopic observations on free droplets we have located different transition lines between 2D fluid smectic phases in (x, T) binary diagrams. In particular a textural criterion has been defined to identify for the first time the $S_{\tilde{C}}$-$S_{\tilde{A}}$ phase transition. Our studies lead to the classification of three 2D fluid smectics according to the following sequence : $S_{\tilde{C}}$-$S_{\tilde{A}}$-$S_{A_{cre}}$ with decreasing temperature.

All smectic A phases are uniaxial mesophases which are constituted of unstructured layers. Referring to some polar systems (pure compounds or binary mixtures) three kinds of S_A-S_A transitions were discovered these last few years : *monolayer* smectic A (S_{A_1}) $\xrightarrow{T\searrow}$ *bilayer* smectic A (S_{A_2}), *partially bilayer* smectic A (S_{A_d}) $\xrightarrow{T\searrow}$ *bilayer* smectic A (S_{A_2}), *partially bilayer* smectic A (S_{A_d}) $\xrightarrow{T\searrow}$ *monolayer* smectic A (S_{A_1}) changes.

In addition to these direct S_A-S_A phase transitions and to the multireentrant NS_A phenomena, intermediate states can occur between two types of smectic A phases [1, 2]. These new mesophases possess a two-dimensional (2D) arrangement due to a long range modulation in the plane of the layers. Nevertheless, in terms of local order they remain smectic with liquid like ordered layers (i.e. *fluid* smectics).

Indeed, cooling from a *monolayer* smectic phase (S_{A_1}) or a *partial bilayer* smectic A phase (S_{A_d}), it is possible to find a 2D oblique lattice (*ribbon phase or tilted fluid antiphase* $S_{\tilde{C}}$) before the condensation of the *bilayer* smectic A phase (S_{A_2}) [3, 4].

Sometimes the S_{A_1}-S_{A_2} change requires a second intermediate phase with a 2D centred rectangular lattice (*fluid antiphase* $S_{\tilde{A}}$) [5]. This sequence can be even more complex with the appearance of a third additional phase (*crenelated* S_A phase : $S_{A_{cre}}$) between the $S_{\tilde{A}}$ phase and the S_{A_2} phase. A. M. Levelut [6] has shown that the $S_{A_{cre}}$ has a 2D simple rectangular lattice.

In fact, at short range order the $S_{\tilde{C}}$, $S_{\tilde{A}}$, $S_{A_{cre}}$ phases are very close to the bilayer smectic arrangement, but these structures are broken periodically by defect walls.

On the basis of microscopic observations on free droplets we have located different transition lines in (molar fraction x, temperature T) binary diagrams.

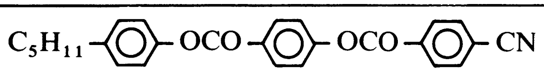
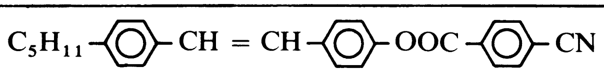
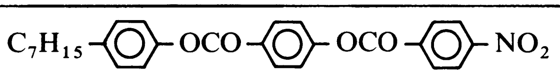
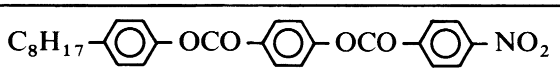
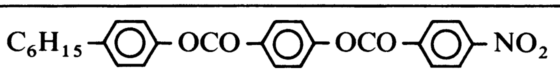
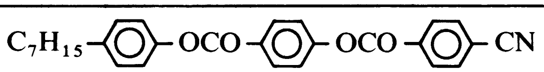
A thin droplet of a given sample is deposited on a glass slide and its free surface is observed between crossed polarizer and analyser ($\times$ 400) in an homeotropic configuration.

These microscopic observations are made in the temperature range of the (x, T) binary diagrams where the fluid mesophases exist.

S_{A_1}-$S_{\tilde{A}}$-$S_{A_{cre}}$-S_{A_2} sequence

By mixing 4-(pentylphenylbenzoyloxy)-4-cyanobenzoate (DB5) with 4-cyanobenzoyloxy-4′-pentylstilbene (C5 stilbene) (see formulae in Table I) the first example of a S_{A_1}-$S_{\tilde{A}}$-S_{A_2} sequence was found [5]. In this original paper we pointed out that the S_{A_1}-$S_{\tilde{A}}$ transition involved characteristic lines of defects which develop and strengthen with decreasing temperature. Then the $S_{\tilde{A}}$-S_{A_2} change occurred through what appeared (at this time) to be a transient texture, made of small domains which join together and finally disappear in S_{A_2} phase. In fact recent results [7] have shown that this new evolving texture is connected to an additional $S_{A_{cre}}$ phase.

Table I.

Acronym	Formula
DB5	
C5 stilbene	
DB7 NO_2	
DB8 NO_2	
DB6 NO_2	
DB7	

Changing the DB5 compound, textural similarities allow us to confirm for the DB6-C5 stilbene and the DB7-C5 stilbene systems the existence of such a *crenelated* S_A phase, but still in a very narrow range of temperature (Fig. 1). Unfortunately, experimental resolution prevented us from giving the topology of the two possible triple points (S_{A_1}-$S_{\tilde{A}}$-S_{A_2} ; $S_{\tilde{A}}$-$S_{A_{cre}}$-S_{A_2}) recently predicted in the frame of a mean field theory by L. G. Benguigui [8].

S_{A_1}-$S_{\tilde{C}}$-$S_{\tilde{A}}$ sequence

The occurrence of a $S_{\tilde{A}}$ antiphase in a pure compound has been clearly shown for the DB7 NO_2 compound by X-ray analysis [9].

In addition we know that the polymorphism is largely modified for the higher homologue (DB8 NO_2) : the high temperature phase is of the S_{A_d} type (instead of S_{A_1}) and the 2D fluid smectic is assigned as $S_{\tilde{C}}$ [3]. The X-ray study of several mixtures of both homologues is consistent with

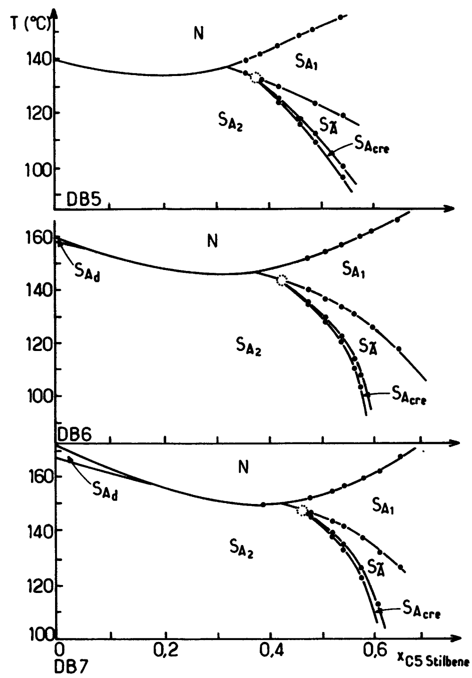


Fig. 1. — (x, T) phase diagrams (P = 1 atm) for the systems : DB5 (left) - C5 stilbene (right); DB6 (left) - C5 stilbene (right); DB7 (left) - C5 stilbene (right).

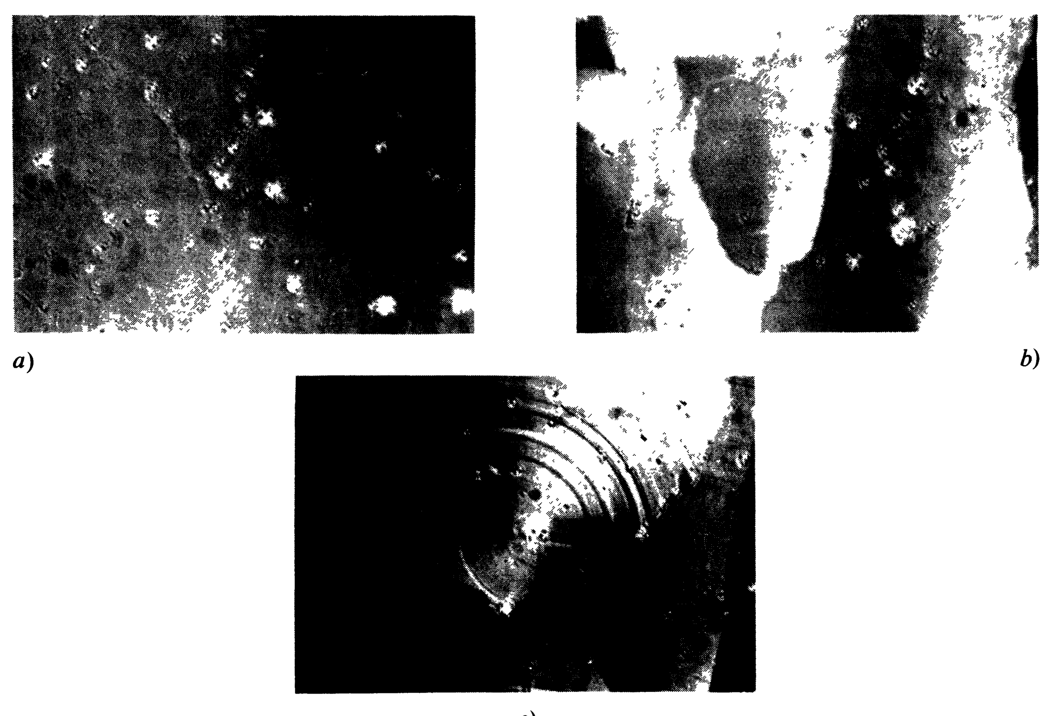


Fig. 2. — Microphotographs taken at different temperatures for the DB7 NO_2 - 0.08 DB8 NO_2 mixture : (a) $T = 95$ °C, S_{A_1}; (b) $T = 92$ °C, $S_{\tilde{C}}$; (c) $T = 90$ °C, $S_{\tilde{A}}$.

a $S_{\tilde{A}}$ being maintained up to a $x = 0.2$ molar fraction of DB8 NO_2 [1]. Regarding the microscopic investigation of these binary mixtures, it is worth noting that the polygonal texture of the $S_{\tilde{C}}$ appears much less birefringent when it arises from a S_{A_1} that when it follows the S_{A_d}. Even in these situations where the $S_{\tilde{C}}$ texture has disrupted the homeotropy, the improvement in our experience in the microscopic observation of free droplets permit the detection of characteristic defects of the $S_{\tilde{A}}$ phase when it exists. The occurrence (or the vanishing) of these defects upon cooling (or heating) at a given temperature over the $S_{\tilde{C}}$ texture give evidence for a reversible $S_{\tilde{C}} \underset{T\nearrow}{\overset{T\searrow}{\rightleftarrows}} S_{\tilde{A}}$ transition (Fig. 2). This essential criterion has been used to reveal a line for the $S_{\tilde{C}}$-$S_{\tilde{A}}$ transition temperatures in the binary diagrams of homologous compounds of the DB_n NO_2 series (Fig. 3). Another connected result is that the $S_{\tilde{C}}$ still exists in a narrowing range of temperature for the pure DB7 NO_2 (over 2 °C) and for the pure DB6 NO_2 (over 0.2 °C).

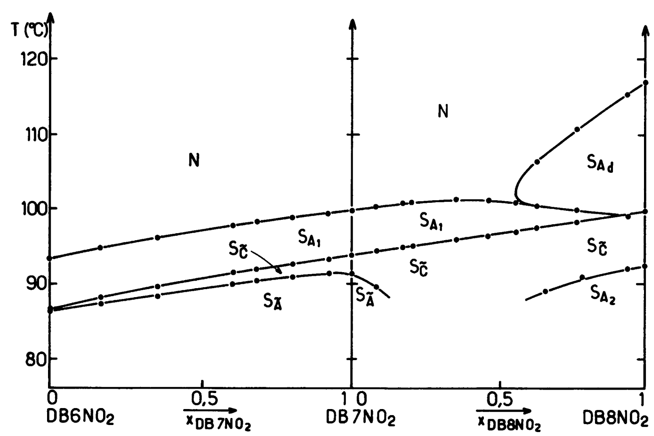
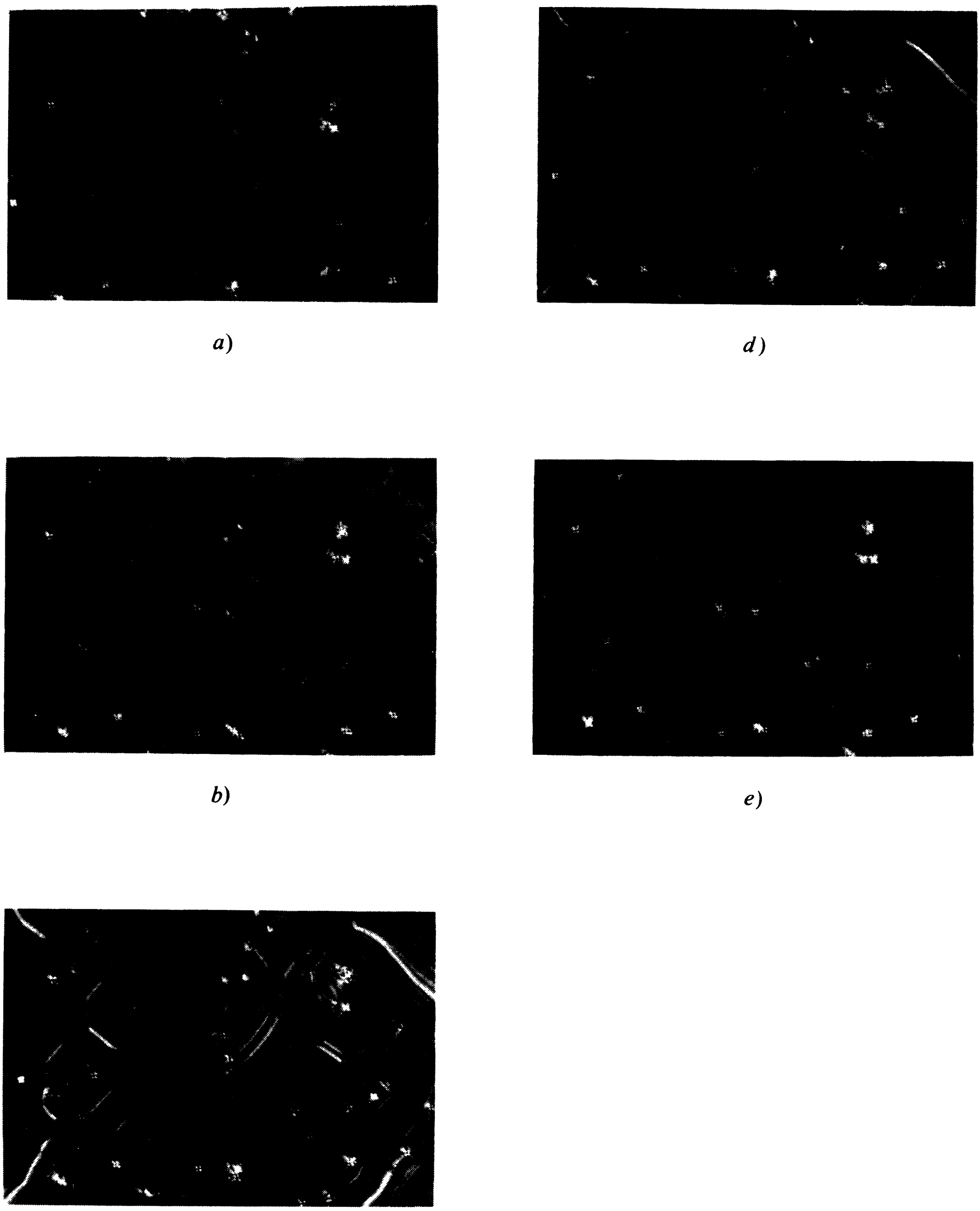


Fig. 3. — Successive (x, T) phase diagrams ($P = 1$ atm) for the systems : DB6 NO_2 - DB7 NO_2 and DB7 NO_2 - DB8 NO_2.

S_{A_1}-$S_{\tilde{A}}$-$S_{\tilde{C}}$-$S_{A_{cre}}$-S_{A_2} sequence.

Keeping in mind previous results, we have considered mixtures of DB7 NO_2 with small amounts of DB7 in order to stabilize a S_{A_2} phase at lower temperatures. By analogy with our microscopic criteria reported here we have detected the following changes with decreasing temperature from the nematic phase : first, the homeotropic aspect of the S_{A_1} phase (Fig. 4a), second the $S_{\tilde{C}}$ textures (Fig. 4b) in which appear at a given temperature the lines of defects characteristic of the $S_{\tilde{A}}$ phase (Fig. 4c), then the textures of the $S_{A_{cre}}$ develop (Fig. 4d) and at last the homeotropic alignment takes place again in the S_{A_2} phase (Fig. 4e). The part of the diagram corresponding to this polymorphism is depicted in figure 5. As mentioned earlier, we stress that the narrow temperature interval of the $S_{A_{cre}}$ phase appears to be a necessary step between $S_{\tilde{A}}$ (or $S_{\tilde{C}?}$) and the S_{A_2} phase. To conclude, this extension of the sequences of 2D fluid smectics between S_{A_1} and S_{A_2} phases will certainly be difficult to confirm by high resolution X-ray and calorimetric experiments considering the studies performed on DB7 NO_2 [10, 11].



a) d) b) e) c)

Fig. 4. — Series of microphotographs taken at different temperatures for the DB7 NO_2 - 0.09 DB7 mixture : (a) T = 103.5 °C, S_{A_1}; (b) T = 100.5 °C, $S_{\tilde{C}}$; (c) T = 96.5 °C, $S_{\tilde{A}}$; (d) T = 94.5 °C, $S_{A_{cre}}$; (e) T = 94.0 °C, S_{A_2}.

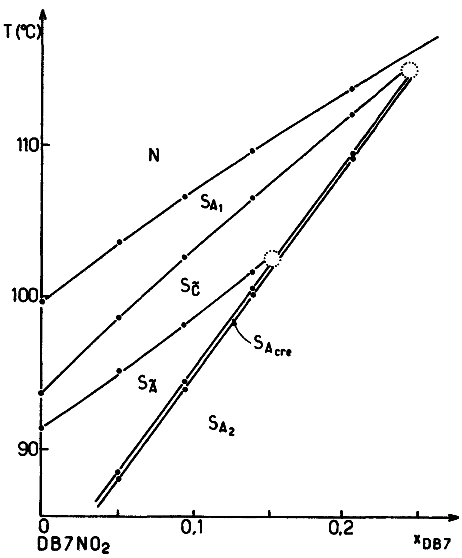


Fig. 5. — Part of the phase diagram for the system DB7 NO_2 (left) - DB7 (right), $0 < x_{DB7} < 0.25$.

References

[1] HARDOUIN, F., LEVELUT, A. M., ACHARD, M. F., SIGAUD, G., *J. Chim. Phys.* **80** (1983) 53 and references therein.

[2] GRAY, G. W., GOODBY, J. W. G., *Smectic Liquid Crystals* (1984) 143-148 (Leonard Hill Ed., Glasgow and London ; Heyden and Son Inc., Philadelphia, USA).

[3] HARDOUIN, F., NGUYEN HUU TINH, ACHARD, M. F., LEVELUT, A. M., *J. Physique Lett.* **43** (1982) L-327.

[4] NGUYEN HUU TINH, HARDOUIN, F., DESTRADE, C., *J. Physique* **43** (1982) 1127.

[5] SIGAUD, G., HARDOUIN, F., ACHARD, M. F., LEVELUT, A. M., *J. Physique* **42** (1981) 107.

[6] LEVELUT, A. M., *J. Physique Lett.* **45** (1984) L-603.

[7] SIGAUD, G., HARDOUIN, F., ACHARD, M. F., *Phys. Rev. A* **31** (1985) 547.

[8] BENGUIGUI, L. G., to be published.

[9] HARDOUIN, F., SIGAUD, G., NGUYEN HUU TINH. ACHARD, M. F., *J. Physique Lett.* **42** (1981) L-63.

[10] SAFINYA, C. R., CHIANG, L. Y., *Bull. Am. Phys. Soc.* **28** (1983) 333.

[11] HUANG, C. C., LIEN, S. C., DUMRONGRATTANA, S., CHIANG, L. Y., *Phys. Rev. A* **30** (1984) 965.