ANOMALOUS TRANSITIONAL BEHAVIOUR IN MIXTURES OF LIQUID CRYSTALS : A NEW TRANSITION OF SA-SA TYPE ?

G. Sigaud, F. Hardouin, M. Achard, H. Gasparoux

ANOMALOUS TRANSITIONAL BEHAVIOUR IN MIXTURES OF LIQUID CRYSTALS : A NEW TRANSITION OF S_A-S_A TYPE ?

G. SIGAUD, F. HARDOUIN, M. F. ACHARD and H. GASPAROUX

Centre de Recherche Paul-Pascal
Domaine Universitaire, 33405 Talence Cedex, France

Résumé. — L'analyse de diagrammes binaires dans lesquels certaines caractéristiques des transitions nématique-smectique A échappent aux théories de McMillan est présentée. Une comparaison des observations microscopiques et de mesures enthalpiques conduit à supposer l'existence de transitions S_A-S_A liée à la structure mono- ou bimoléculaire des couches smectiques.

Abstract. — The study of binary diagrams for which some features of the nematic-smectic A transitions are not in agreement with McMillan's theories is presented. A comparison of microscopic observations with enthalpic measurements leads to assume the occurrence of S_A-S_A transitions, the structure of smectic layers being either monomolecular or bimolecular.

1. Introduction.

— Temperature-concentration phase diagrams for binary mixtures have demonstrated for a long time their utility, first in the characterization of mesophases by isomorphism [1] but also in the comparison with molecular or phenomenological models. For this purpose, the analysis of physical properties such as magnetic anisotropy, enthalpies of transition, viscosities in two component mixtures has been proved to be very useful [2, 3]. These quantities depending either on the order parameter variations or critical fluctuations allowed to test [4] the theories of N-S_A transitions or to confirm the existence of very peculiar points (or domains) appearing in some diagrams (tricritical *Landau* point [2], N-S_A-S_C so called Lifshitz point [5], reentrant nematics [6]).

Nevertheless, some anomalies and new theoretical arguments [7] require the reexamination of established data especially about the nematic to smectic A transition. We present here a study of these peculiar cases and some observations which do not seem to be explained by the current theories.

2. Previous results and exceptions.

— The studies we have performed up to now about the N-S_A transitions using pure compounds as well as mixtures (in addition to numerous other works [8, 9]), seem to be in very good agreement with the theories proposed by McMillan [10] and De Gennes [11]. Peculiarly, the evolution of the first order character of the transition to a second order one with regard to the decrease of the T_{NA}/T_{NI} parameter seems confirmed. It is moreover evidenced as previously predicted by the theories [10], that for values of this ratio lower than 0.87 approximatively (reached only in mixtures) the type of transition is really second order.

Nevertheless, this satisfactory coherence seems to be challenged by Lubensky and Meyer arguments [7] according to which a N-S_A second order transition could not always be related only to this T_{NA}/T_{NI} ratio. To support their statements, the authors take the example of the 4-n pentylphenyl-4-[4-cyanobenzoyl-oxy] benzoate [12] (« dibenzoate » for short) :

Its polymorphism would be the following :

$$\text{Isotropic} \rightleftarrows \text{Nematic} \rightleftarrows \text{Smectic A}$$

with

$$T_{NI} = 249 \, °C, \qquad T_{NA} = 139 \, °C.$$

Consequently, the ratio T_{NA}/T_{NI} is 0.78 although a first order thermodynamical character has been observed at the nematic to smectic transition.

After synthetizing this compound in our laboratory we have performed enthalpic and magnetic anisotropy measurements. We find indeed a relatively high enthalpy at the

$$\text{N-S transition} = 472 \text{ mcal mole}^{-1} \text{ K}^{-1}$$

and we detect a slight magnetic anisotropy discontinuity at this phase change (Fig. 1). Nevertheless, one can notice the weakness of this increase in anisotropy compared to the value of the latent heat (by comparison, $\Delta H_{CBOOA} \simeq \Delta H_{dibenzoate}/8$; anisotropy comparison is given on figure 1).

These measurements confirm the first order character of this transition but also show that, although the orientational order is almost saturated, the transitional enthalpy is large.

Thus, an ordinary coupling between orientational and translational orders seems to be inadequate to describe this case. To explain these peculiar experi-
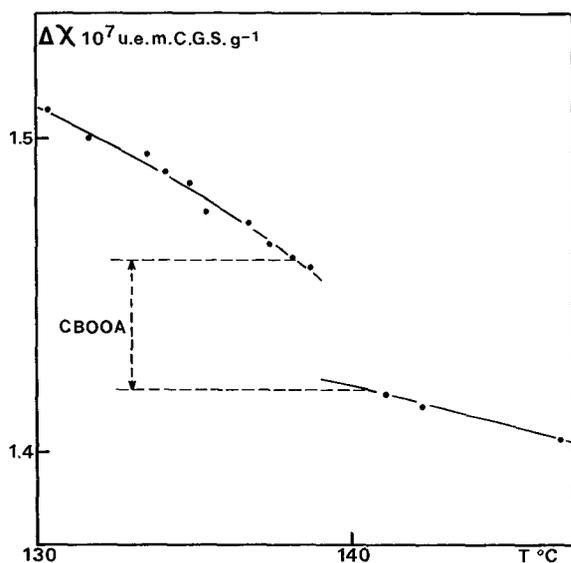
FIG. 1. — Thermal variation of the dibenzoate magnetic anisotropy around the nematic to smectic transition. Comparison with CBOOA.
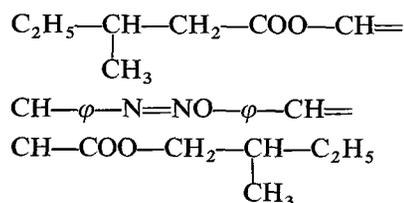
mental results, it is then necessary to answer two important questions :

Is it truly a nematic to smectic A transition ?

If it is, are the arguments proposed by Meyer and Lubensky relevant in this case ?

3. **Characterization of the smectic phase.** — With regard to textures, this phase presents a strong tendency to homeotropy : this suggests an uniaxial structure. Focal conic textures are also observed. This is in agreement with a S_A phase. By contact method we have identified this mesophase to known smectics A presenting compatible temperature ranges :

Total miscibility was found with the S_A phase of the following compound (Fig. 2) :

$$C_2H_5—\underset{\underset{CH_3}{|}}{CH}—CH_2—COO—CH=$$

$$CH—\varphi—N=NO—\varphi—CH=$$

$$CH—COO—CH_2—\underset{\underset{CH_3}{|}}{CH}—C_2H_5$$

as well as with the TBBA one (Fig. 3).

Moreover, the diagram drawn using mixtures with heptyloxy-benzilidene-p-aminofluorenon shows a $N \rightarrow S \rightarrow S_C$ sequence of transitions which can be understood only if the phase comprised between the nematic and the smectic C is a smectic A (Fig. 4).

By means of isomorphism, the smectic phase of dibenzoate is undoubtedly of smectic A type.

4. **Study of the dibenzoate/TBBA diagram.** — To determine why the T_{NA}/T_{NI} ratio has a different meaning for this compound, we have taken interest in the N-S_A transitions which arise along the equilibrium curves of the figure 3 (dibenzoate/TBBA diagram).
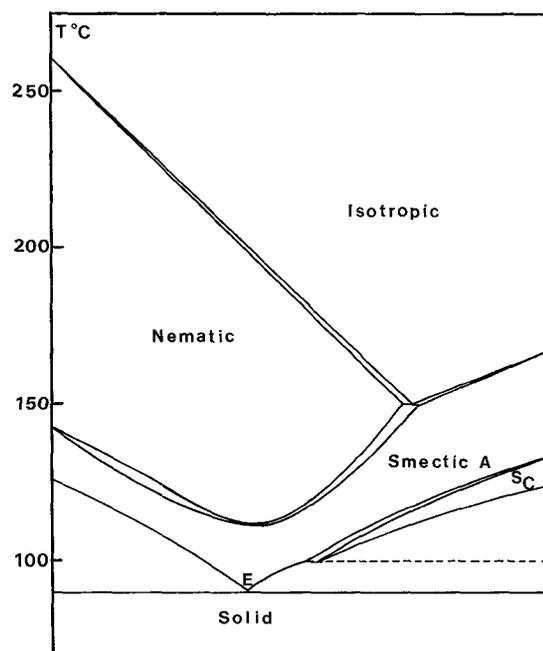

FIG. 2. — (x, T) isobaric phase diagram for binary system : dibenzoate (left) azoxy compound (see text) (right). Contact method.
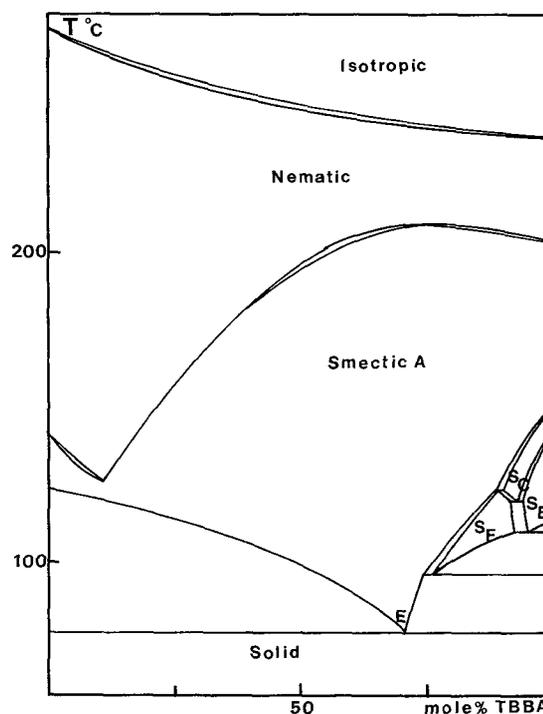

FIG. 3. — (x, T) isobaric phase diagram for binary system : dibenzoate (left) TBBA (right). Contact method.

By observation of successive mixtures, we have precisely drawn the two branches (1 and 2) which flank the minimum located at $x_{TBBA} = 0.12$ (Fig. 5). One can notice that a ratio $T_{NA}/T_{NI} = 0.74$ corresponds to this extremum and that this parameter increases on each side to reach 0.78 for pure dibenzoate and to exceed the 0.87 boundary on the branch 1.
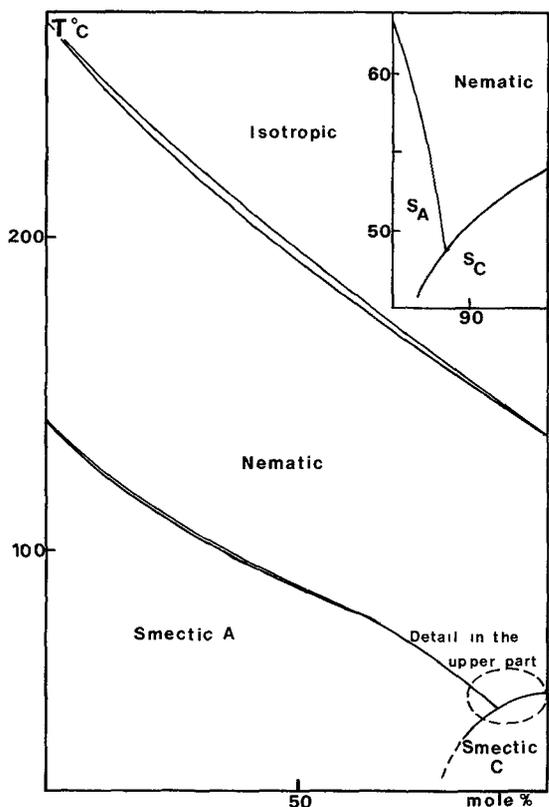
FIG. 4. — (x, T) isobaric phase diagram for binary system : dibenzoate (left) heptyloxy benzilidene aminofluorenon (right). Contact method. Enlarged detail : microscopic observation of successive mixtures.

For the same mixtures, we have measured the transitional enthalpies using a Du Pont 990 DSC.

The figure 6 presents the results connected with the branch 1 for $x_{TBBA} > 0.25$. For high values of the T_{NA}/T_{NI} ratio we detect a latent heat : the transition is first order. When this ratio decreases, the enthalpy decreases too and then vanishes at a point where the ratio $T_{NA}/T_{NI} = 0.875$ agrees with a *classical* behaviour. Further, within the accuracy of the apparatus, the N-S_A transitions can be considered as 2nd order.
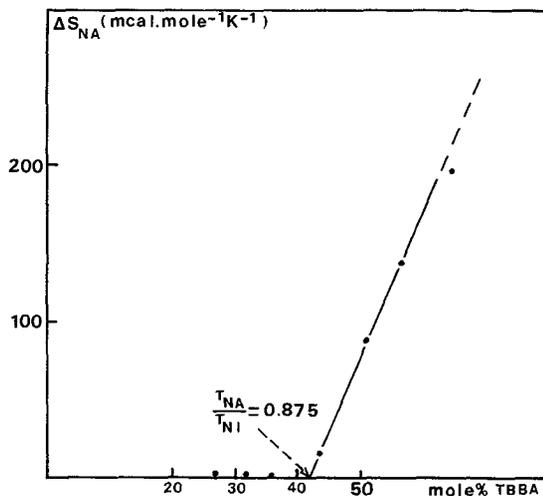

FIG. 6. — N-S_A transitional entropies for $x_{TBBA} > 0.25$.

The entropy evolution along the branch 2 is presented on figure 7. When one approaches the minimum in the diagram, this quantity decreases dramatically but does not vanish at this point. Moreover, if we
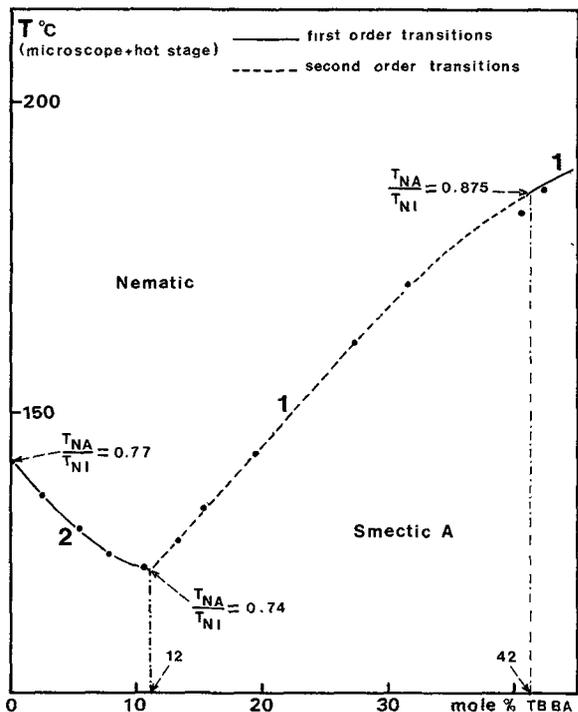

FIG. 5. — Detail of dibenzoate (left)/TBBA (right) binary diagram near the minimum. Microscopic observation of successive mixtures.
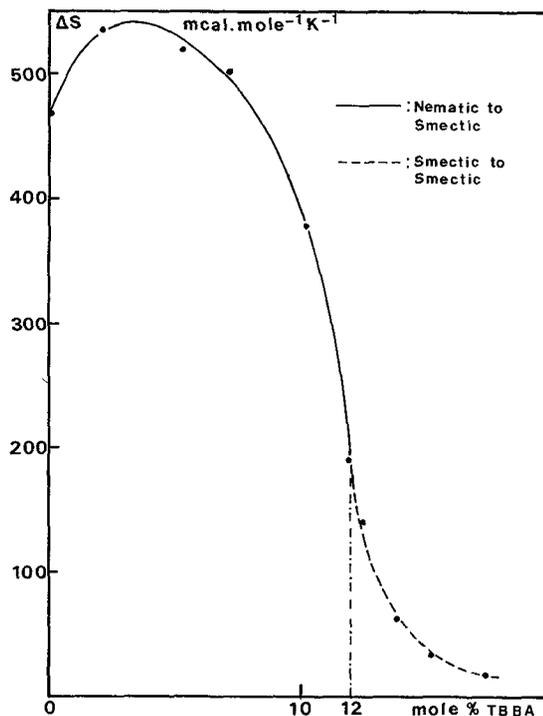

FIG. 7. — Entropies of transition for $x_{TBBA} < 0.20$.

perform further enthalpic measurements increasing the TBBA molar fraction $(0.12 < x_{TBBA} < 0.25)$ it appears two successive transitions on the thermal analysis :

— The high temperature one (necessarily a nematic-smectic one) for which the temperature is identical to the one observed by microscopic way is detected only by a little increase of the specific heat.

— The second (a smectic-smectic one) appears at lower temperature with a measurable latent heat. Entropy evolution versus the molar fraction (dotted line on figure 7) seems to be the prolongation of the entropy variation of the N-S transition along the branch 2 (full line on figure 7).

From these thermal investigations, we can thus draw the diagram of figure 8 : the two branches on each side of the minimum are superposable to the ones determined by microscopy but it appears a third line of weakly first order transitions which in no way can be observed optically.

5. **Conclusion.** — These results lead us to propose the following explanation : in the described part the dibenzoate/TBBA diagram consists of :

— a line of $N \to S_{A1}$ transitions the features of which are in agreement with De Gennes' and McMillan's descriptions ;

— a line of $N \to S_{A2}$ transitions which does not follow the evolution criterions with regard to the T_{NA}/T_{NI} parameter (all these transitions are observable by microscopy) ;

— a line of transitions which necessarily corresponds to a $S_{A1} \to S_{A2}$ change, impossible to detect optically. Such a behaviour might be explained if we consider the fact that the layers in the S_A phase of the dibenzoate present a bimolecular organization stronger than the one of the octyloxy cyanobiphenyl 8OCB : this is confirmed by XR measurements for which two peaks are clearly visible (A. M. Levelut, private communication). On the other side, the TBBA presents a structure with monomolecular layers. Thus, the $S_{A1} \to S_{A2}$ transition could perhaps cor-
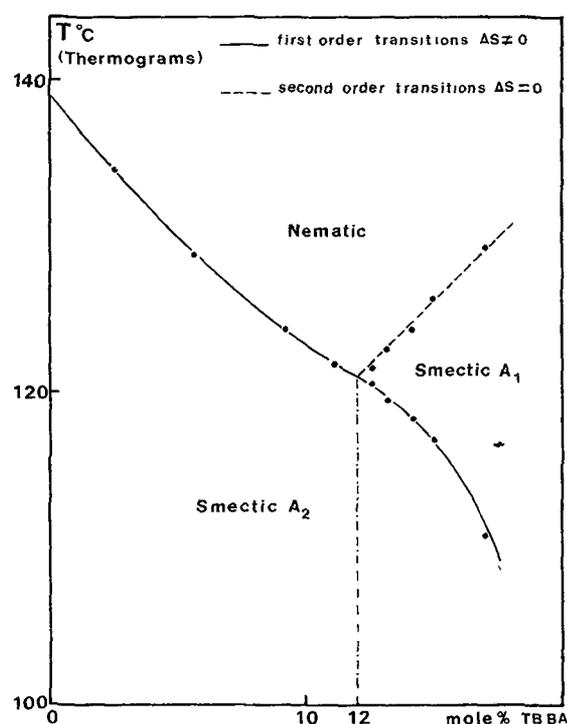

Fig. 8. — Part of dibenzoate (left)/TBBA (right) diagram drawn from the thermograms (DSC).

respond to the transformation of a smectic A with monomolecular layers into a smectic A with bimolecular layers. Preliminary, XR intensity results seem to be consistent with such a transition (A. M. Levelut, private communication). Perhaps, is it thus necessary to define different types of smectic A ? At last, it is suggested that the theories should take in account the effects due to the bimolecularity. Such a proposal is consistent with the approach of Meyer and Lubensky who consider in the expansion of the molecular density an additional order parameter which represents the tendency for molecules to pack in half spaced layers. A Landau theory which involves these arguments will be soon presented elsewhere (J. Prost, to be published).

References

[1] SACKMANN, H., DEMUS, D., *Mol. Cryst.* 2 (1966) 81.
[2] HARDOUIN, F., SIGAUD, G., ACHARD, M. F., GASPAROUX, H., *Solid State Commun.* 22 (1977) 343.
[3] ACHARD, M. F., GASPAROUX, H., HARDOUIN, F., SIGAUD, G., *J. Physique Colloq.* 37 (1976) C3-107.
[4] HARDOUIN, F., Thesis, Univ. Bordeaux I (1978).
[5] SIGAUD, G., HARDOUIN, F., ACHARD, M. F., *Solid State Commun.* 23 (1977) 35.
[6] CLADIS, P. E., *Phys. Rev. Lett.* 35 (1975) 48.

[7] MEYER, R. B., LUBENSKY, T. C., *Phys. Rev.* A 14 (1976) 2307.
[8] DOANE, J. W., PARKER, R. S., CVIKL, B., JOHNSON, D. L., FISHEL, D. L., *Phys. Rev. Lett.* 28 (1972) 1694.
[9] KEYES, P. H., WESTON, H. T., DANIELS, W. B., *Phys. Rev. Lett.* 31 (1973) 628.
[10] McMILLAN, W. L., *Phys. Rev.* A 4 (1971) 1238.
[11] DE GENNES, P. G., *Solid State Commun.* 10 (1972) 753.
[12] VAN METER, J. P., KLANDERMAN, B. H., Fourth International Liquid Crystal Conference, Kent, Ohio, August 1972.