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## PRESSURE STUDIES ON LIQUID CRYSTALLINE MATERIALS

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**Résumé.** — On a étudié l'effet de pressions modérées (quelques kilobars) sur le polymorphisme de quelques cristaux liquides, et notamment :

- a) un mésomorphisme induit par la pression dans les acides méthoxy- et éthoxybenzoïques ;
- b) l'élimination d'une phase smectique C par la pression dans le 4,4'-bis (heptyloxy) azoxybenzène ;
- c) le comportement tricritique du cholestéryl oleyl-carbonate confirmant le travail de Keyes *et al.*

**Abstract.** — Recent results on the effect of pressure on phase transitions in liquid crystalline materials are described. The following observations are presented :

- a) Pressure induced mesomorphism in methoxy- and ethoxybenzoic acids.
- b) Disappearance of the smectic C phase in 4,4'-bis(heptyloxy) azoxybenzene at high pressure.
- c) Tricritical behaviour in cholesteryl oleyl carbonate, confirming an earlier report of Keyes, Weston and Daniels.

We report here some results from our recent studies on the effect of pressure on phase transitions in mesomorphic materials. A single-acting hydraulic press (100 tons with 4" diameter movable piston or, for higher pressures, 1 000 tons with 10" diameter piston) was used for the experiments. The phase transitions were detected by differential thermal analysis (DTA). An important feature of the pressure cell was that the sample was completely enclosed and sealed in a teflon capsule, so that there was no possibility of decomposition or of contamination by the pressure transmitting

medium, which in this case was talc. Pressures were calibrated by means of a standard manganin pressure gauge, following the method described by Jayaraman *et al.* [1]. Further details of the experimental arrangement have been reported elsewhere [2, 3]. In the data given below each experimental transition point is the average of at least two DTA runs taken at different heating rates. That the sample was free from decomposition or contamination was confirmed by the reproducibility of the transition temperature at atmospheric pressure, after the completion of the experiment.

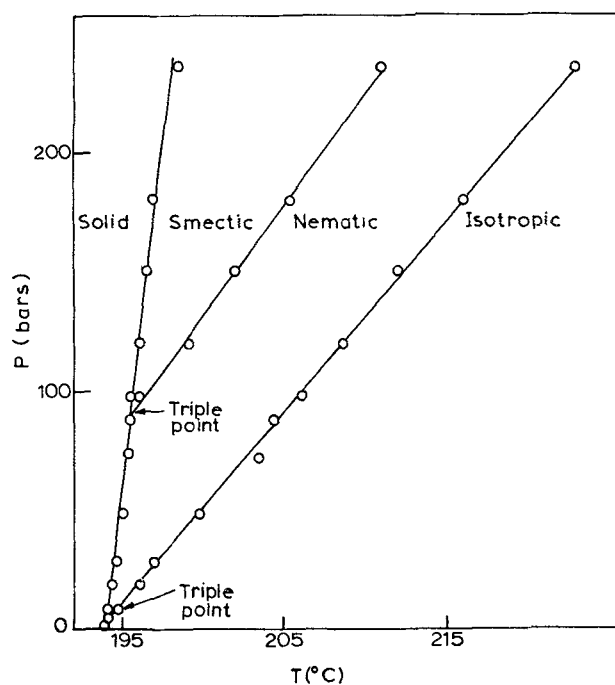


FIG. 1. — Experimental phase diagram for methoxybenzoic acid.

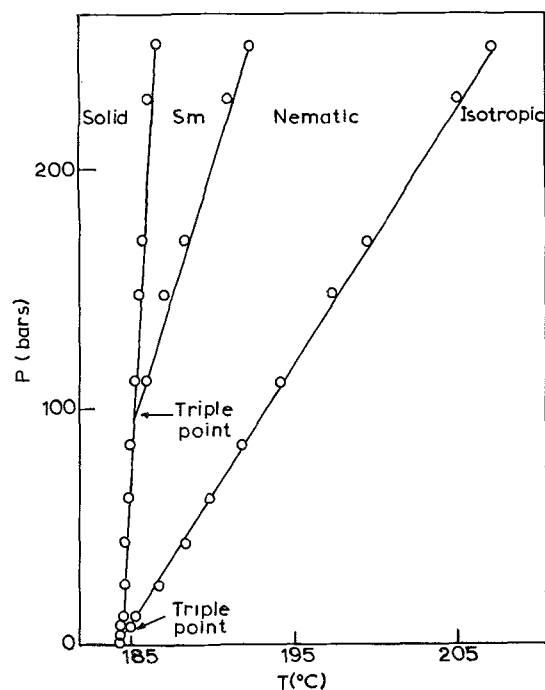


FIG. 2. — Experimental phase diagram for ethoxybenzoic acid.

**1. Pressure induced mesomorphism.** — We first describe observations of mesomorphism induced by pressure in compounds that are non-mesomorphic at atmospheric pressure. These studies were undertaken to verify a conclusion drawn from phase diagrams evaluated by means of the Pople-Karasz theory of melting [2]. Experiments were conducted on two compounds which just miss being mesomorphic at atmospheric pressure, namely, methoxy- and ethoxy benzoic acids, the first two members of the p-n-alkoxy-benzoic acid series.

Both compounds exhibit similar behaviour under pressure (Fig. 1 and 2). At atmospheric pressure there is just a single transition, the solid-liquid melting transition. As the pressure is raised both compounds show mesophases, initially a nematic phase and then, at higher pressures, a smectic phase as well. The pressure induced phases were identified by microscopic observation of their textures using a specially designed optical cell [4]. These experiments have established for the first time the existence of the solid-nematic-isotropic and solid-smectic-nematic triple points in single component systems.

**2. 4,4'-Bis(heptyloxy) azoxybenzene.** — Figure. 3 shows the P-T diagram for 4,4'-bis(heptyloxy) azoxybenzene. At atmospheric pressure, this compound exhibits the crystalline, smectic C, nematic and isotropic phases. As the pressure is increased, the range of the smectic phase diminishes until, at a pressure of about 6.68 kbar, it disappears altogether. By contrast with the results described in section 1, this is an interesting example of the suppression of a mesophase by pressure. A possible explanation for this behaviour is that the tilt

angle in the smectic C phase increases on application of pressure until at sufficiently high pressures the layered structure is lost completely and the solid transforms directly to the nematic phase.

**3. Cholesteryl oleyl carbonate.** — We present in figure 4 the raw DTA records of the smectic A-cholesteric transition in cholesteryl oleyl carbonate, at different

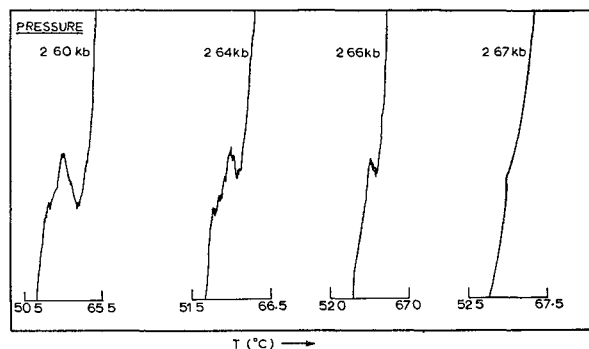


FIG. 4. — DTA records of the smectic A-cholesteric transition in cholesteryl oleyl carbonate at different pressures.

pressures in the neighbourhood of 2.65 kbar. It is seen that as the pressure is raised the first order character of the transition gradually diminishes and becomes practically second order at about 2.67 kbar. Thus the compound appears to show a *tri-critical* point, though we should emphasize that with the sensitivity of our apparatus we cannot assert unequivocally that it is in fact a truly second order transition at this pressure. The phase diagram for this compound is shown in figure 5.

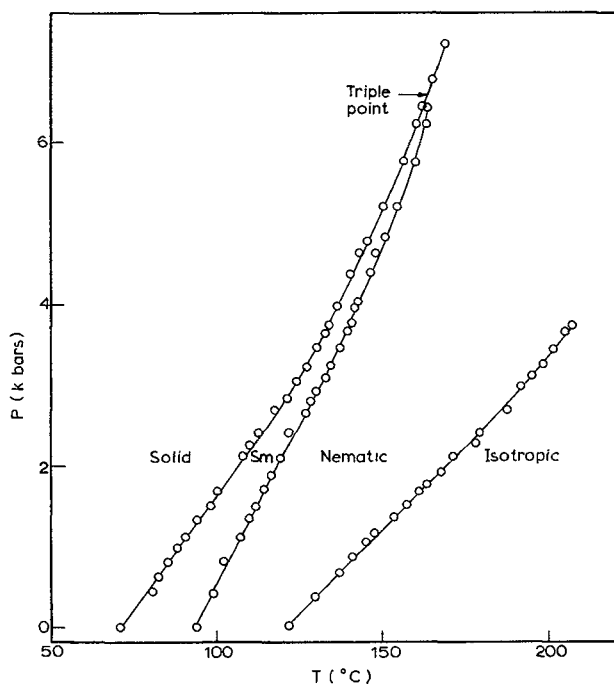


FIG. 3. — Experimental phase diagram for 4,4'-bis(heptyloxy) azoxybenzene.

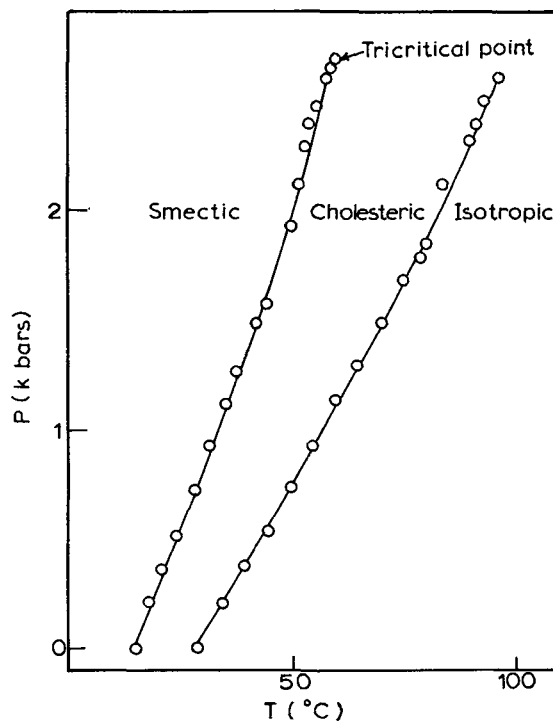


FIG. 5. — Experimental phase diagram for cholesteryl oleyl carbonate.

Our observations confirm the results of Keyes *et al.* [5], who have studied the phase transitions in the same compound by measuring the attenuation of transmitted light as a function of pressure. From the least squares fit of their data, they find a tri-critical point at 2.66 kbar and 60.3 °C, in excellent agreement with our data.

Further studies are in progress. In particular, the discovery of pressure induced mesomorphism in methoxy- and ethoxybenzoic acids has encouraged us

to explore the possibility of observing liquid crystalline behaviour in *normal* organic liquids composed of shorter molecules, by subjecting them to very high pressures.

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#### References

- [1] JAYARAMAN, A., HUTSON, A. R., MCFEE, J. H., CORIELL, A. S. and MAINES, R. G., *Rev. Sci. Instruments* **38** (1967) 44.
- [2] CHANDRASEKHAR, S., RAMASESHAN, S., RESHAMWALA, A. S., SADASHIVA, B. K., SHASHIDHAR, R. and SURENDRANATH, V., *Proceedings of the International Liquid Crystals Conference, Bangalore, December 3-8, 1973* (to be published).
- [3] RESHAMWALA, A. S., SHASHIDHAR, R., CHANDRASEKHAR, S. and RAMASESHAN, S. (to be published).
- [4] SHASHIDHAR, R., CHANDRASEKHAR, S. and RAMASESHAN, S. (to be published).
- [5] KEYES, P. H., WESTON, H. T. and DANIELS, W. B., *Phys. Rev. Lett.* **31** (1973) 628.