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Piezothermal studies in the vicinity of the smectic A-nematic transition in 4'-n-octyloxy-4-cyanobiphenyl (8OCB)

R. Shashidhar (*)⁽¹⁾, L. Ter Minassian (**), B. R. Ratna (***) and A. N. Kalkura (***)

(*) Department of Chemistry, Institute of Physical Chemistry,
University of Bochum, 4630 Bochum, Federal Republic of Germany

(**) Laboratoire de Chimie Physique, Université Pierre et Marie Curie,
11, rue Pierre et Marie Curie, 75231 Paris Cedex 05, France

(***) Raman Research Institute, Bangalore-560 080, India.

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Résumé. — L'expansion thermique (α) de 4'-n-octyloxy-4-cyanobiphényle (8OCB) a été étudiée en fonction de la pression sur différentes lignes isothermes par la méthode piézothermique. A proximité de la transition α smectique A-nématique apparaît une anomalie qui devient moins prononcée lorsque la température augmente.

Abstract. — The thermal expansion (α) of 4'-n-octyloxy-4-cyanobiphenyl (8OCB) has been studied as a function of pressure along different isotherms by the piezothermal method. In the vicinity of the smectic A-nematic transition, α shows an anomaly which becomes less pronounced with increasing temperature.

1. **Introduction.** — Although the first observation of the re-entrant nematic behaviour in a pure compound was at high pressure [1], the subsequent observation of this behaviour at atmospheric pressure [2] has led to the fact that most of the experimental studies that are being conducted on re-entrant nematogens are almost exclusively atmospheric pressure experiments. In fact, apart from the p - T diagrams of Cladis *et al.* [1, 3], the only other studies at high pressure on re-entrant nematics are an X-ray [4] study and some A.C. calorimetric studies [5, 6]. We report here measurements on the thermal expansion (α) of 4'-n-octyloxy-4-cyanobiphenyl (8OCB) as a function of pressure along 4 different isotherms by the piezothermal method.

2. **Experimental.** — The piezothermal or heat of compression method [7, 8] essentially consists of a measurement of a quantity of heat Q liberated by a volume V_s of the sample under a pressure variation of Δp . This quantity of heat is directly related to the thermal expansion coefficient α of the sample by the relation [9, 10] :

$$Q = -(\alpha - \alpha_r) TV_s \Delta p, \quad (1)$$

⁽¹⁾ Humboldt fellow and on leave of absence from the Raman Research Institute, Bangalore-560 080, India.

where α_r is the expansion coefficient of the containing material. The calorimeter used is a conventional flux calorimeter (SETARAM) adopted for high pressure experiments. The experimental set up which is the same as that used earlier for the study of the thermal expansion of water and some organic liquids, has already been described elsewhere [7, 8] and will not be repeated here. Essentially, the sample, contained in a pressure tubing and suspended inside the calorimeter, is compressed. The resulting heat liberated in the sample is measured as an emf by a set of 500 thermocouples which are electrically in series but thermally in parallel. The combined emf of the thermocouples is recorded and integrated as a function of time. The area under the « thermogram » [7] gives the quantity of heat Q caused by a change of pressure Δp . The apparatus having been initially calibrated using an ideal gas like nitrogen (see reference [7] for details regarding the calibration procedure used), i.e. α_r and V_s being pre-determined, α of the sample can be determined using equation (1). The absolute pressures and temperatures were measured to accuracies of ± 0.5 bar and ± 0.01 K respectively. They were also maintained to the same accuracies. The relative accuracy in the determination of α is reckoned to be about $\pm 2\%$.

3. Results and discussion. — The sample of 8OCB used in the present study was purchased from BDH England and was used without further purification. The transition temperatures at 1 bar were 67.0°C for the smectic A-nematic (A-N) and 81.0°C for the nematic-isotropic (N-I) transitions. The p - T diagram, obtained using an optical cell [11], is given in figure 1. The maximum pressure of occurrence of the smectic A phase is 1.98 kbar which is in good agreement with the earlier data of Cladis *et al.* [1] and Garland *et al.* [5]. The experiment has been conducted along 4 different isotherms, viz., 68.7 , 71.4 , 75.1 and 77.6°C . Before commencing the experiment at any temperature, the system was allowed to attain thermal equilibrium for at least 24 hours. Then the pressure was increased very slowly to a pressure of about 200 bar above the A-N transition pressure at that temperature. Pressure was then decreased by small steps (a few bars) and the

Fig. 1. — p - T diagram for the smectic A-nematic transition of 8OCB. The dashed lines indicate the temperatures at which the measurements of α have been made.

Fig. 2. — Variation of the thermal expansion (α) of 8OCB with pressure at 4 different isotherms : (a) 68.6 °C ; (b) 71.4 °C ; (c) 75.1 °C and (d) 77.6 °C.

area of the potential *versus* time curve integrated at each step. Initially, at pressures not close to the A-N transition, the time necessary for each step was about 40 min. However, in the vicinity of the A-N transition the recording and integration had to be carried out for much longer periods of time. No experiments could be conducted on the re-entrant nematic phase owing to the rapid crystallization of the supercooled smectic A phase.

Figures 2(a)-(d) show the thermal expansion *versus* pressure curves for the 4 different temperatures studied. α exhibits an anomaly at the A-N transition. The strength of this peak decreases with increasing temperature and at the highest temperature studied, *viz.*, 77.6 °C, there is hardly any anomaly (Fig. 2(d)). Generally, it is far more difficult to achieve as fine a variation of pressure as of temperature. To that extent, we would like to emphasize that our experimental values of α , particularly close to the A-N transition, do not have the precision required to make a good estimate of the exponent (β) associated with the pressure variation of α . Nevertheless, an attempt has been made to fit all the data points for $T = 68.6$ °C to equations of the type :

$$\alpha = a_0 + p_r a_1 + A |p_r|^\beta, \quad \text{for } p < p_0$$

and

$$\alpha = a_0' + p_r a_1' + A |p_r|^\beta, \quad \text{for } p > p_0,$$

where a_0 , a_1 , a_0' and a_1' are all adjustable parameters, p_0 is the A-N transition pressure for

$$T = 68.6^\circ\text{C},$$

$p_r = |(p - p_0)|/p$ is the reduced pressure. The base lines with respect to which the expansion coefficients have been evaluated for this fitting consist of two linear parts, one in the nematic and the other in the smectic A phases. The data points at pressures farthest from p_0 have been used to obtain these two linear base line parts which intersect at the A-N transition pressure p_0 . This appears to yield a reasonably good fit over the entire range of pressure investigated, giving a value of 0.22 for the exponent β . Attempts were also made to fit the same set of data points in another manner, i.e., by taking the two base line parts to have a discontinuity (and not intersect) at p_0 . Such a fitting procedure gave a very poor fit, indicating thereby that the A-N transition may be more aptly described as a higher order transition than a first order one.

It may also be mentioned that an integration of the α versus pressure curve essentially leads to a term which should be a function of entropy (see e.g. Ref. [7]). Thus it is not surprising that the trends of our α versus pressure curves with increasing temperature resemble generally the C_p versus temperature curves with increasing pressure obtained for the same compound by Garland *et al.* [5, 6]. A detailed thermodynamic analysis of our piezothermal data is being carried out and will be published separately.

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