Pressure Dependence of the Nematic State Temperature of a Compensated Cholesteric Liquid Crystal

Optical Rotatory Power Measurements with a Cholesteryl chloride and Cholesteryl nonanoate Mixture

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At a certain temperature T_n (nematic temperature) a mixture of two cholesteric components which separately form helices of opposite senses behaves like a nematic. An inversion of the helical structure occurs when passing T_n, from a right-handed to a left-handed structure or vice versa. In the temperature-pressure space such compensated mixtures therefore will exhibit an inversion line which — on the basis of optical rotatory power measurements under high pressure — is presented for the first time.

The cholesteric structure of certain liquid crystals can be converted to nematic by application of electric or magnetic fields (see e.g. [1]). That means that the helical arrangement of the long molecular axes turns into a parallel one. This effect can be observed, however, without the influence of such fields: for instance at the phase transition point cholesteric/smectic [2], or by mixing two cholesteric components which separately form helices of opposite senses. At a certain temperature T_n (nematic temperature) such a cholesteric liquid crystal behaves like a nematic (see e.g. [3], measurements at atmospheric pressure). Moreover, an inversion of the helical structure occurs when passing T_n, from a right-handed to a left-handed structure or vice versa.

In the temperature(T)-pressure(p) space such compensated mixtures therefore will exhibit an inversion line, the theoretical interest of which already having been mentioned by Papoular in 1969 [4]. The experimental determination of this inversion line requires the measurement of the pressure dependence of T_n, which is presented in this paper for the first time.

Approaching T_n at constant p, or p_n (nematic pressure) at constant T, the pitch of the cholesteric helix increases to infinity prior the inversion. — The pitch can be determined by the measurement of the wavelength of maximum light reflection λ_0. — This method, often used in our high pressure investigations of the cholesteric structure (see e.g. [2]) is in our experimental case limited to pitches of about 2000 nm. To find $T_n(p_n)$ the observation of higher pitch values is necessary. Therefore we have studied the optical rotatory power (OR) of a compensated cholesteric mixture. This OR is mainly a structural rotation and related to the helical molecular arrangement. It is orders of magnitude higher than that of the constituting molecules. For a high-pitch (z) cholesteric structure (measuring wavelength λ less than λ_0) according to De Vries [5] the specific rotation α_0 can be expressed by

$$\alpha_0 = (360/8\,\lambda^2)\,(\Delta n)^2\,z\,, \tag{1}$$

where Δn is the birefringence of the local nematic orientation. Since α_0 is proportional to z, it also goes through infinity at T_n and p_n, respectively, and changes sign as does the sense of the helical screw.

Our OR measurements were done with a 64.6/35.4 mole mixture of cholesteryl chloride (right-handed helix) and cholesteryl-n-nonanoate (left-handed helix). The sample was contained between silica disks separated by a lead spacer of 25 μm. The disks were treated with an etheric solution of lecithin before introducing the sample. The OR was observed on the basis of the half shadow method. Details of the high pressure optical cell will be published later. The angle of rotation was measured as a function of pressure at constant temperature. Figure 1 shows an example for 69.20 °C and displays an ending of the two parts of the isotherm in some distance from the nematic pressure p_n. What is the reason for this behaviour? The OR of a cholesteric structure is a defined property only as long as the liquid crystal forms a plane texture. In the case of untreated disks, already in some distance from p_n the plane texture changes into the schlieren texture and no further measurement of the OR is possible. The pressure range, where the schlieren texture appears, is too large for determining p_n in this way, and moreover, the reproducibility is unsufficient. Therefore the sample disks were treated with an etheric solution of lecithin. The consequence of this treatment is the following:

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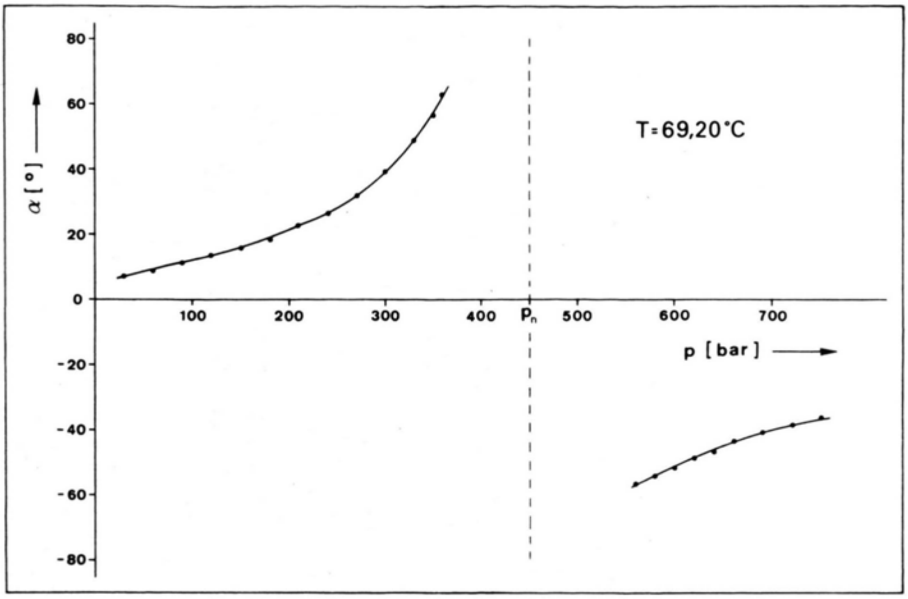

Fig. 1. Optical rotatory power α as a function of pressure p at temperature $T = 69.20\,^{\circ}\mathrm{C}$ of a 64.6/35.4 mole mixture of cholesteryl chloride/cholesteryl nonanoate. Measuring wavelength $\lambda = 530$ nm.

In some distance from p_n now the fingerprint texture is observed and again no measurement is possible, however the occurence of the succeeding homeotropic texture near p_n (when $z \sim$ layer thickness [6]) can be detected sharply by the polarimeter ($\alpha = 0$). When forming the homeotropic texture the long axes of the molecules switch from a parallel to a normal orientation to the disk surface. The pressure interval where this orientation is obtained, is about 10 bars. The advantage of treating the disks

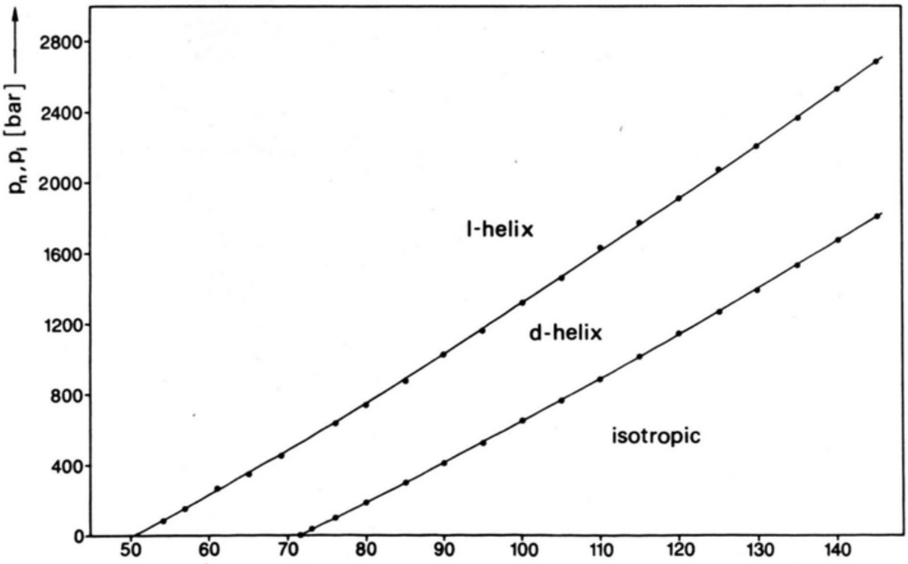

Fig. 2. Nematic pressure p_n as a function of nematic temperature T_n (inversion line l-helix/d-helix) and isotropic transition pressure p_i as a function of isotropic transition temperature T_i, respectively, of a 64.6/35.4 mole mixture of cholesteryl chloride/cholesteryl nonanoate.

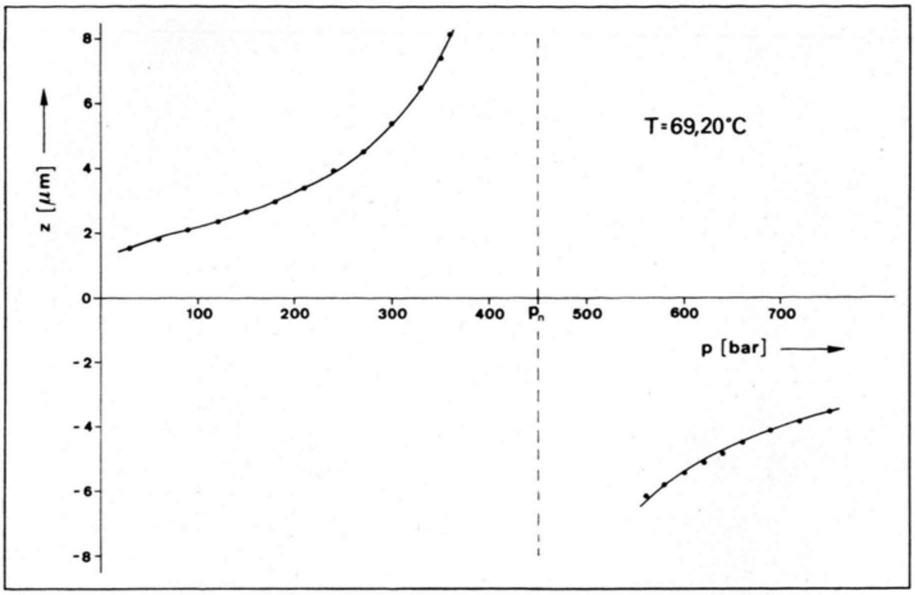

Fig. 3. Pitch z of the cholesteric helix of a 64.6/35.4 mole mixture of cholesteryl chloride/cholesteryl nonanoate as a function of pressure p at temperature $T = 69.20\,°C$ calculated from p, T-birefringence data of a nematic [8].

with lecithin is that contrary to experiments with untreated disks the plane texture returns when the sample has passed p_n. Thus both parts of the isotherm (see Fig. 1) can be measured in one preparation.

Former measurements at atmospheric pressure have shown that the pitch changes symmetrically with temperature around T_n [3]*. Since with a given layer thickness the length of the pitch determines the appearance of the homeotropic texture, taking p_n as the middle between the upper and lower point where this texture occurs should be a reliable approximation. The distance between both points increases with temperature and was between 110 and 250 bars. The reproducibility of p_n obtained in the described way is about 10 bars.

p_n as a function of T_n is shown in Figure 2. The inversion curve l-helix/d-helix has a weakly increasing slope with T_n. Since, moreover, the temperature (T_i) dependence of the isotropic transition pressure (p_i) of the CC/CN mixture could be observed, a widening of the d-helix pressure range with temperature can be seen from Figure 2 too.

Calculation of the pitch $z(p)$ at constant T from the experimental angles of rotation of the cholesteric phase according to (1) requires knowledge of the birefringence Δn of the local nematic orientation. Since no p, T-data of Δn of a cholesteric are available, we made use of the measurements of Horn [8] who studied the p, T-dependence of Δn of two nematics up to 2000 bars. As an example the results of the approximate calculation of $z(p)$ at $T = 69.20\,°C$ are presented in Figure 3. The obtained values of z around p_n in Fig. 3 are representative for all temperatures along the inversion line.

Before attempting a theoretical explanation of the observed $p_n(T_n)$-behaviour we will investigate the dependence of this behaviour on the molar fraction of this compensated binary system.

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* Recent measurements [7] have established that this is not strictly the case.

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