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INVESTIGATION OF CHOLESTERYL VALERATE UNDER PRESSURE

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We report the results of an experimental study of the
specific volume of liquid-crystal matter (cholesteryl valer-
ate) at a pressure up to 1000 atm and in the temperature in-
terval 80 - 129°C, including the phase transitions; plots
of the isotherms and the P-T diagram are presented.

Interest in liquid crystals is due to their applications in electronics [1], medicine [2],
and other fields [3, 4], and the temperature interval in which the mesophases exist is of
considerable practical interest.

We have investigated experimentally the behavior of the mesophases under pressure, and
also the nature of the phase transitions between different phases of this class of substances.
We note that in spite of the great theoretical interest there are no published experimental
data on the specific volume of liquid crystals under pressure.

The first such investigations were performed by us on paraazoxyanisole [4], a homolog
of the dialoxyazoxybenzene series, in which only one liquid-crystal (nematic) phase, whereas
cholesteryl valerate has two phases, cholesteric and smectic [5]. The investigation of the
cholesteryl valerate was carried out at pressures up to 1000 atm on 32 isotherms (80 - 129°C),
five of which are shown in Fig. 1 (the 111, 109, 103, and 99°C isotherms are raised in the
figure 0.04, 0.04, 0.06, and 0.07 cm³/g, respectively).

As follows from the figure, with increasing pressure the volume of the isotropic phase
decreases linearly and goes over into the cholesteric phase without any noticeable effect,
apart from an insignificant change of slope. Such a behavior is observed on the majority of
the isotherms, and the transition points shown on the T-P diagram lie on a straight line
given by the expression (Fig. 2a)

$$t°C = 102 + 0.0715P.$$

We note that the behavior of the cholesteric phase under pressure differs little from the
isotropic phase, although under normal conditions this difference is more noticeable [3]. Such
transitions are apparently closed phase transitions [6].

Further increase of the pressure transforms the cholesteric phase into the smectic one.
The transition occurs in some range of pressure (not at a single point), and is well noticed
on all the isotherms (starting with 94°C upwards). The transition temperature increases with
increasing pressure linearly (Fig. 2b) and is described by the expression

$$t°C = 93 + 0.0565P.$$

The sensitivity of the employed setup [3] has enabled us to measure several points within
the limits of the transition (isotherms 119 and 103°C of Fig. 1).

Finally, we measured the specific volume of the smectic phase, whose variation under pres-
sure is patently nonlinear. When temperatures given by the relation (Fig. 2c)

$$t°C = 79.6 + 0.0396P$$

are reached, a transition to the solid-crystal phase sets in and is accompanied by a jump in
the volume. The volumes given for the solid-crystal phase should be regarded as tentative,
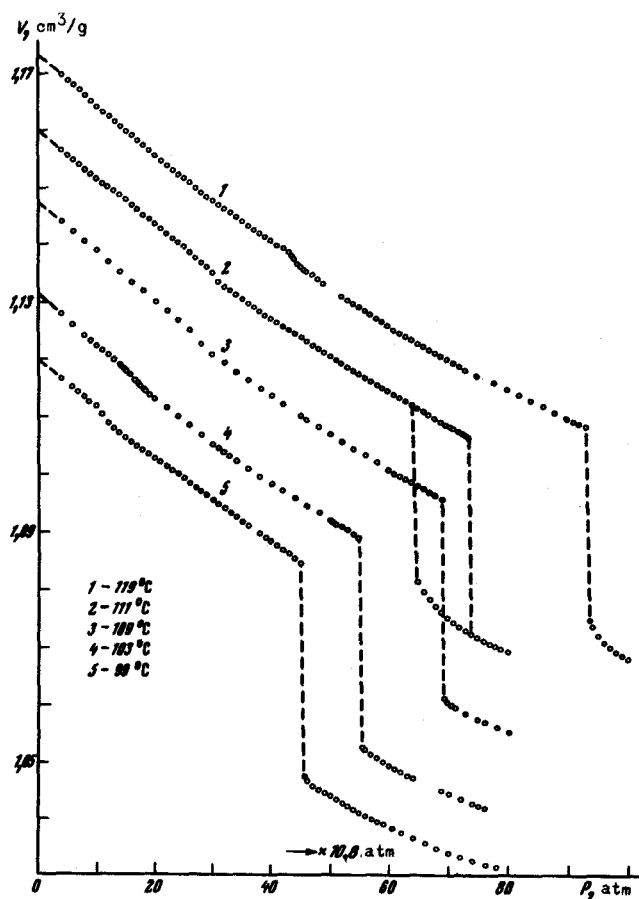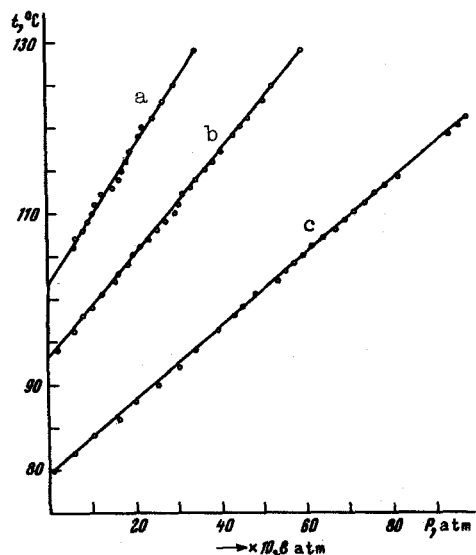since the apparatus was not intended for measurements of solid phases.

Fig. 2. P-T diagram of transitions in cholesterylvalerate: a) isotropic liquid - cholesteric phase, b) cholesteric - smectic phase, c) smectic - solid-crystal phase.

Fig. 1. P-V isotherms of cholesterylvalerate (the 111, 109, 103, and 99°C isotherms are raised 0.04, 0.04, 0.06, and 0.07 cm^3/g, respectively).

The 111°C isotherm was plotted twice, with increasing and decreasing pressure; the obtained hysteresis curve confirms that the transition is of first order.

We can thus conclude that different liquid-crystal phases react differently to pressure: The cholesteric phase is practically linear, whereas the smectic phase is patently nonlinear. This is especially noticeable in our case, since three phase transitions were obtained on a single isotherm. Incidentally, the phase transition from the cholesteric to the smectic phase is very similar to the transition from the nematic to the solid-crystal phase of paraazoxyanisole [7], although the results are more unambiguous for cholesteryl valerate, since the transition takes place between two liquid-crystal phases and the volume effects are measured more accurately.

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