HEATS OF TRANSITION TO THE SOLID AND ISOTROPIC-LIQUID STATES FOR LIQUID CRYSTALS OF p-AZOXYANISOLE AND CHOLESTERYL CAPRINATE

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Calorimetric methods are applied to p-azoxyanisole and cholesteryl caprinate. The heats of conversion to the solid state substantially exceed those for conversion to isotropic liquid. The latter result indicates that liquid crystals are closer to liquids than to solids.

It is sometimes considered that there are only three states of matter (solid, liquid, and gas), but substances that form liquid crystals have a substantially larger number of mutually convertible phases. For example, cholesteryl caprinate (CC) has solid, liquid, and two liquid-crystal forms, leaving aside the vapor form. Moreover, a liquid crystal can have points of stepwise change of texture even within a single liquid-crystal form.

Fig. 1. a) Centers (droplets) in a liquid crystal of PAA; b) solid texture of PAA.

Thermodynamically speaking, the phase transitions of liquid crystals in no way differ from other first-order transitions; they correspond to closed regions on the phase diagram [1]. There are stepwise changes in molecular order at the transition points of liquid crystals, which are confirmed by the occurrence of heats of transition, though these are small relative to heats of melting.

Melting occurs in at least two stages if a liquid is formed. First the solid becomes a liquid crystal, in which the long-range order is lost with respect to the centers of gravity but is retained to some extent with respect to the orientations. Then there is a gradual loss of the orientation order, and the liquid crystal eventually becomes an anisotropic liquid consisting of optically anisotropic liquid-crystal nuclei in an amorphous liquid. Frenkel [2] called this orientation melting. Here I report the heats of transition for both forms of melting.

Very few measurements have been made of these heats. Data have been published on these heats for p-azoxyanisole (PAA), but the numerical values do not agree, especially over the transition points, whereas none have been published for CC. To obtain accurate values, rates of temperature change not exceeding 0.1 deg/min were used.

EXPERIMENTAL

First the texture-transition points for PAA (C_{14}H_{14}N_{2}O_{3}) and CC (C_{37}H_{64}O_{2}) were measured with an MP-6 polarizing microscope fitted with a 60 W biological heater and thermostat. The slide was held by flat springs on a carrier inserted from the side into the heated space, which had a central hole to admit the microscope and another at 12° to the optical axis to admit a T-3 chromel-alumel thermocouple capable of measuring to 0.01°. The lower hole was closed by a glass slide, while the entire heated system was protected from convection by a cardboard jacket. The contrast was improved by the use of a blue filter.

Fig. 2. a) Centers of smectic phase in the cholesterol phase of CC; b) texture of smectic phase of CC; c) centers of solid CC crystals.
The heater was supplied with ac via an ST-750 stabilizer, the current being adjusted by two calibrated rheostats (coarse and fine) giving respectively 50 and 0.1 mA/div. The fine control allowed the heating or cooling rate to be made as low as 0.02 deg/min.

The transition points and texture changes were examined visually and by recording with a Zenith-S camera in polarized light or in natural light.

Some of the specimens were also examined in glass tubes immersed in a liquid bath. The transition points were again recorded with a T-3 thermocouple. Although the rate of change of temperature in a ±5° range around the transition point was as in the other method (0.1 deg/min), there was some difference in the values found for the transition point, most of the points found in this second method being 0.92° above the others. The main reason is that the mass of material in the tube was 250 times that on the stage; also, the pressure in the tube increased on heating.

The heats of transition were measured calorimetrically. The calorimeter was insulated by two layers of foam plastic in a tufnol cylinder. The specimen (1.5 g) in a glass tube was heated to 5° above the transition point and then was cooled to that point, at which it was kept for 30 min before transfer to a calorimeter containing 45 ml of distilled water. This 30 min period reduced the temperature difference at both walls of the tube to 0.14°. The specimen was kept in the calorimeter for 60 min, after which the heat release H2 was determined. Then the tube was heated again to the transition point, kept there for 30 min, and returned to the calorimeter, the heat release H2 being measured after 60 min. The difference ΔH = H1 − H2 is the heat released by the transition. The detailed results are given below.

The main source of error is radiative loss, and its magnitude was determined from the known heats of fusion for cinnamic acid (m. p. 133°), resorcinol (110°), α-naphthol (95°), naphthalene (60°), and thymol (50°). The limits of error for PAA and CC at their transition points were ±7% and ±5% respectively.

An isotropic melt of PAA on cooling to 136° is converted to a liquid crystal; the heat of transition was found as 0.72 cal/g. At 115.45° there are produced droplets (centers) (Fig. 1a) that move about and join up. The entire material is converted to this form (a fatty drop) at 114.20°. The measured heat of transition to the solid state was 28.33 cal/g at this transition point.

This texture underwent a sudden change at 101.8° (Fig. 1b), after which it remained unchanged. This effect is well seen on cooling at 0.05 deg/min. An analogous effect, but at 103°, has been reported for PAA. The difference in value is to be ascribed to differences in cooling rate, which in the case of [3] was 0.2 deg/min, whereas I used 0.1 deg/min.

An isotropic melt of CC on cooling to 90.6° is converted to a liquid crystal (cholesterel phase); the heat of transition was measured as 0.74 cal/g. Liquid crystals of the smectic phase became visible at 83.14° (Fig. 2a); at 82.75° these fused into a single fatty drop. The heat of transition was measured as 0.87 cal/g. A blue color appears when this modification is formed, and this can be seen over the range 83.92°-82.75°. The texture of the smectic phase becomes coarser when the blue color vanishes. There is some change in the texture at 73.40°, which is accompanied by swirling and production of an orange-yellow color, which is seen over the range 75.68-73.4°, below which the texture becomes finer (Fig. 2b). The heat of transition at 73.4° was found as 13.30 cal/g. The color changes in the phase transitions would appear to point to some shifts in the molecular energy levels.

The texture shown in Fig. 2b persists unchanged down to 61.80°, below which solid crystals grow (Fig. 2c). The heat of transition at this point is 16.71 cal/g.

Chistyakov [4] has deduced similar transition points for CC from the transmission curve; the discrepancies are to be ascribed to differences in the rate of temperature reduction.

Values have been given [5] for the heat of transition of p,p'-azoxyanisole to the liquid state from a liquid crystal and to the solid state from the latter (0.69 and 28.2 cal/g). Here again there was some difference in the transition points.

The many results for transition points quoted in [6, 7] differ by much more than 1°; there are also differences in the heats of transition. The discrepancies are due not only to the methods of measurement but also to the methods of making the crystals. However, in all cases the heat of conversion to the liquid from the liquid crystal is small.

CONCLUSIONS

1. Heats of transition from the liquid state to the liquid crystal have been measured for PAA and CC (0.72 cal/g ±7% and 0.74 cal/g ±7%), as have the heats for transition from the liquid crystal to the solid state (28.33 cal/g ±5% and 16.71 cal/g ±5%); in addition, the heat of the polymorphic transition within the smectic modification of CC at 73.4° has been measured as 13.30 cal/g ±5%.

2. The heats of solidification greatly exceed the heats for conversion of the liquid crystal to the liquid state.

3. The very low values for the latter heats show that liquid crystals resemble liquids more closely than solids.

REFERENCES

