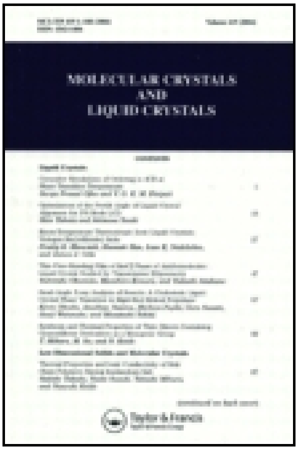

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Pressure Dependence of the Pitch of Cholesteryl Oleyl Carbonate

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Pressure Dependence of the Pitch of Cholesteryl Oleyl Carbonate

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Pollmann and Stegemeyer[1] have shown that the pitch of a cholesteric mixture of cholesteryl oleyl carbonate (COC) and cholesteryl chloride (CC) increases very rapidly with pressure, approaching infinity at a critical pressure p_c whose value depends on the composition of the mixture. At first sight, this result is surprising as one would anticipate only slight "red shift" when the sample is compressed. The aim of this note is to show that the observed critical divergence is in fact to be expected from theoretical considerations.

COC exhibits a smectic A-cholesteric transition at 14°C. The cholesteric pitch P increases rapidly as the temperature approaches this transition, the temperature dependence being expressible as[2,3]

$$P - P_0 = A(T - T_c)^{-\nu} \tag{1}$$

where P_0 is the intrinsic pitch in the absence of a smectic phase and T_c is the apparent second order smectic A-cholesteric transition point.

In the present problem the temperature is constant (at room temperature T_R) but the transition point T_c rises with pressure so that the pitch exhibits a critical divergence. The critical pressure p_c is that pressure at which $T_c = T_R$. The pressure dependence of the pitch may be calculated approximately as follows:

In pure COC, T_c increases linearly with pressure over the range 0–1.60 kbar.[4] Assuming that the same type of linear variation is present in the mixtures also Eq. 1 may be expressed as

$$P - P_0 = B(p_c - p)^{-\nu} \tag{2}$$

Unfortunately, we have no reliable estimate of P_0 for the mixtures. To overcome this difficulty we shall assume that the dependence of P_0 on pressure in the small range of interest near p_c is negligible and write

$$\frac{\partial(P - P_0)}{\partial p} \simeq \frac{\partial P}{\partial p} = B\nu(p_c - p)^{-\nu-1}. \tag{3}$$

We have estimated $\partial P/\partial p$ from the experimental curve of Pollmann and Stegemeyer;[1] a log–log plot of $\partial P/\partial p$ versus $(p_c - p)$ is approximately linear. For one mixture (COC/CC = 80.1/19.9 mole %) the slope of the line is -1.70, or $\nu = 0.7$ (Figure 1).

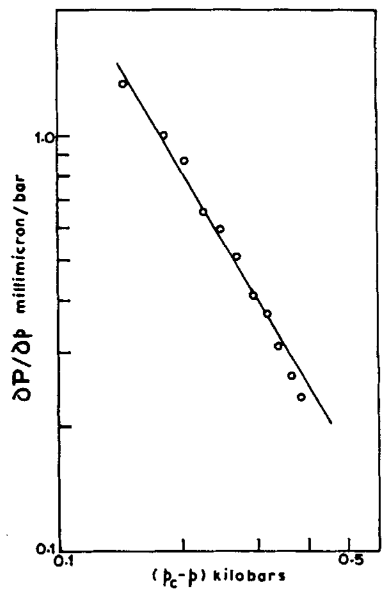

FIGURE 1 Log–log plot of $\partial P/\partial p$ versus $(p_c - p)$ for a mixture of cholesteryl oleyl carbonate and cholesteryl chloride (80.1/19.9 mole %). The slope of the line is $-(\nu + 1) = -1.70$ or the critical exponent $\nu = 0.70$. The critical pressure $p_c = 900$ bars.[1]

A similar plot for the other mixture (COC/CC = 74.8/25.2 mole %) gives $\nu = 0.9$. The actual slope depends rather sensitively on the value of the critical pressure p_c, which for this mixture has been reported to be 1500 bars. This emphasizes the fact that not much reliance can be placed on the values of the critical exponent ν till accurate experimental estimates of P_0 and p_c are available. However, the calculation does bring out the essential reason for the rapid increase of the pitch of COC with pressure.

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