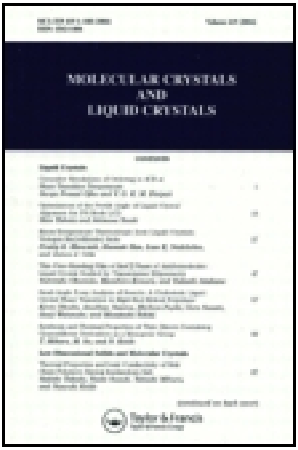

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V. N. Alexandrov [a] & I. G. Chistyakov [a]

[a] Pedagogical Institute of Iwanowo, USSR

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The Optical Activity of the Mixtures of *p*-Azoxyanisole and Cholesteryl Propionate‡

V. N. ALEXANDROV and I. G. CHISTYAKOV

Pedagogical Institute of Iwanowo
USSR

Abstract—The optical activity of *p*-azoxyanisole and cholesteryl propionate as a function of wavelength, temperature and particularly of the concentration of the active substance has been studied. For small concentrations (about 1% propionate) the deviation from linearity of the activity *versus* the reverse titre has been observed. For mixtures of about 1% propionate one can say there is saturation.

In this paper the optical activity of mixtures with 20, 15, 5, 2.5, 1.5 and 1 per cent of the propionate has been studied as a function of temperature, wavelength and particularly concentration of the active component (propionate).

The cholesteric mesophase has a number of unique optical properties.[1] These include enormous optical activity[2] attaining in some cases up to 10^5 degrees per mm. It is interesting to note, also, that in mixtures of the cholesteric and nematic substances the optical activity grows as the quantity of the active constituent falls.[3] But only in the recent works of Cano and Chatelain[4,5] have the qualitative characteristics of this phenomenon been established. They have given an elegant and simple theoretical explanation of this phenomenon based on the works of Mauguin[6] and de Vries.[7]

The optical activity of such mixtures has been found to be a linear function of the inverse concentration of the active

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component. On the other hand the current concept of the cholesteric structure as a helicoidally twisted one with a pitch P_c together with the assumption that mixing of a cholesteric substance with a nematic one gives simply a " dilution " of the cholesteric structure (i.e. the non-active nematic molecules persist to align themselves parallel to each other and only the active molecules of the cholesteric mesophase cause twisting of the medium) lead them to the following results.[4,5] Twisting of a mixture on 2π will give a specimen with such a height P_m (and unit area), that it would persist to contain a permanent quantity of a cholesteric substance, equal to that quantity which would give twisting of the medium on one turn in a pure cholesteric substance. If the densities of the mixed substances differ only slightly, the ratio of the pitch of the pure cholesteric compound to that in the mixture will be equal to the concentration of the active material, i.e. the pitch of the mixture is proportional to the inverse concentration.

But the theory of Mauguin[6] and of de Vries[7] connect the optical activity with the value of the pitch. For wavelengths sufficiently small with respect to the pitch (as usually takes place in sufficiently diluted mixtures over the whole visible region) the optical activity is proportional to the value of the pitch, i.e. is inversely proportional to the concentration of the active material.

This concept has had very good agreement with experimental data[2,4,5] in the region of the concentrations of the active material from 20 to 5 per cent. But intuitively it seems very unlikely that this proportionality of the optical activity to the inverse concentration can last over a large concentration range. The main purpose of our work was the investigation of the optical activity as a function of concentration of the active substance for as small a concentration as possible.

The substances we chose were *p*-azoxyanisole (PAA) with transition points at 117 °C and 134.6 °C and cholesteryl propionate with transition temperatures at 97.5 °C and 112 °C. The latter compound has only the cholesteric mesophase. Its optical activity has been studied by Mathieu.[8] According to his results the propionate is a *levo* substance with an inversion wavelength about 458 mμ displaced to longer wavelengths at lower temperatures. All our mixtures were also *levo* in the whole visible region.

The optical activity was measured by the usual method with a polarizing microscope. A monochromator was used as a light source and the spectral slit-width did not exceed 70 Å in the red region. The error of the method is estimated to be about 5 per cent. For a more detailed description of the method of measurement see, for example, reference (9).

In most cases the calculations were made from four rings and the average was taken from $\binom{4}{2} = 6$ values. We succeeded in measuring the optical activity of the mixtures up to 1 per cent of the propionate (for the mixtures of 20, 15, 5, 2.5 and 1 per cent). The results are shown in Fig. 2. The optical activity is given everywhere in radians per mm. In all the Figures (except Fig. 2) we use the reduced temperature, i.e. the optical activities of different mixtures were compared by temperature in equidistant points from their isotropic transition points (Fig 1). Temperatures in Figs. 3 and 4 are relative to the pure PAA.

The relative optical activity was computed for all mixtures. (The value of the optical activity for some wavelengths has been taken as unity and the other wavelength values for the same temperature are expressed as fractions of this value. The same procedure is repeated for the remaining temperatures.) As with Cano's results it was found independent of the temperature (and less precisely of the concentration). It seemed interesting to us to try to establish the correlation between the optical activity of the mixtures with small concentrations and the degree of orientation for the pure PAA. In other words, we tried to find combination which would be a simple function of the temperature. The best results were obtained for the combination $\rho/S \log 1/S$ (S = degree of orientation). It is almost linear in the region of the reduced temperatures from 100° to 130°. These results are given in Fig. 3.

Control measurements of the double refraction of the pure PAA were made. The difference in the visual pattern from that

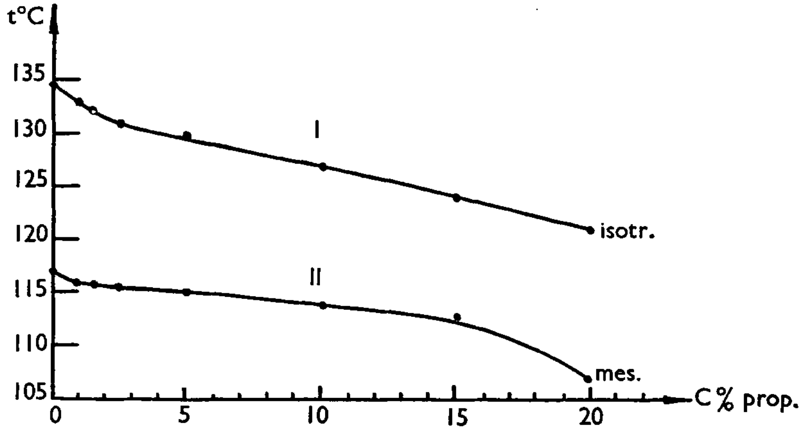

Figure 1. The transition temperatures from liquid crystal to liquid (curve I) and solid to liquid crystal (curve II) for the mixtures versus propionate concentration.

in active mixtures is clearly seen even for the 1 per cent mixture. The rings are more narrow and the difference in their conduct at an analyzer turning is easily identified. Computed values of the double refraction were compared with those given by Chatelain and Germain.[10] The discrepancy did not exceed 5.9 per cent (one point out of twelve which were compared, the remainder 4 per cent and less). Several " optical activities " formally computed from measured rings of the double refraction for the pure PAA gave values which were 4–5 times more than the ones for the 1 per cent mixture.

The curves of the optical activity *versus* the inverse concentration are shown in the Fig. 4. There are deviations from the straight line for small concentrations of the active substance. Thus we can speculate about a peculiar saturation for the 1 per cent mixture. It should be noted that for small concentrations the errors of the measurements increase by reason of non-controlled variations of concentration from one specimen to another, which are here relatively more pronounced. But on the other hand it has a small effect on the shape of the curve because in the region of less than 1.5 per cent it is almost parallel to the x-axis.

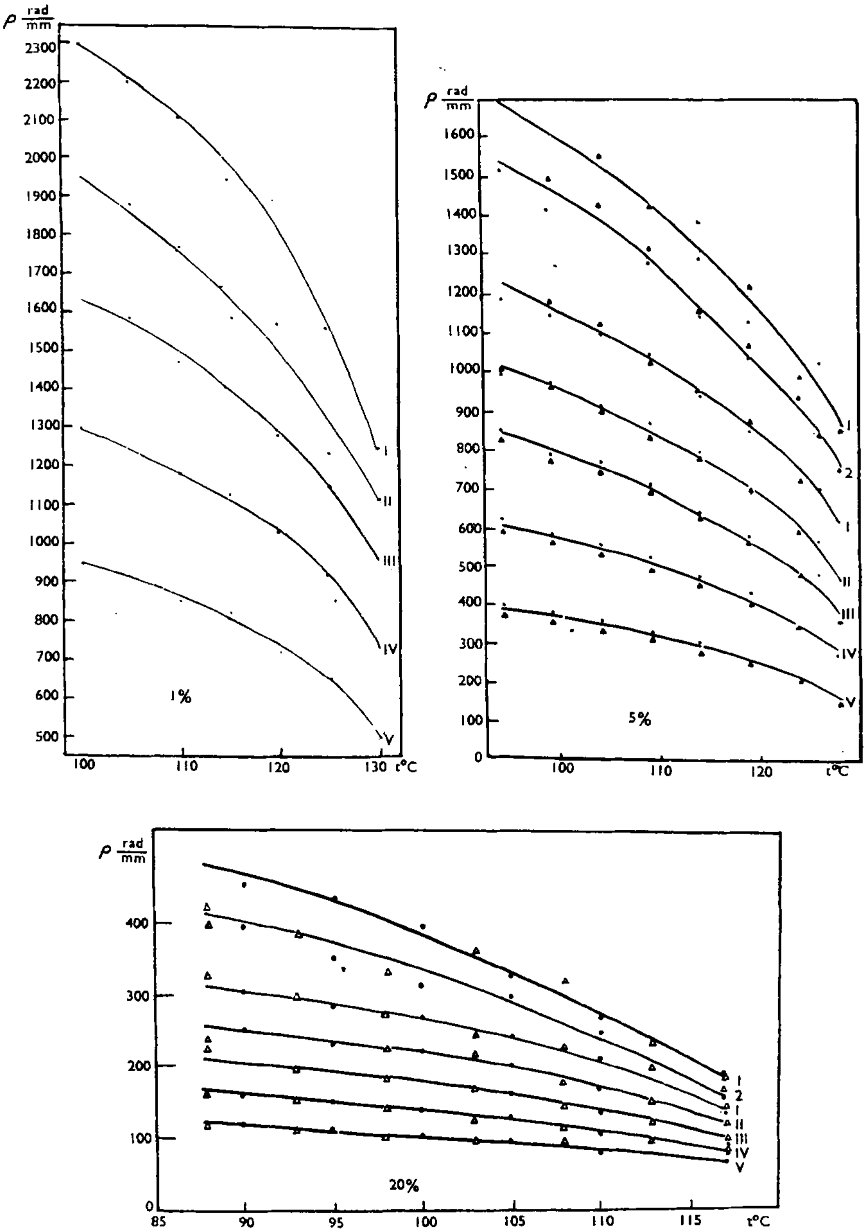

Figure 2a, b, c. Optical activity of different mixtures *versus* temperature for different wavelength (1-4460 Å, 2-4545 Å, I-4710 Å, II-4890 Å, III-5130 Å, IV-5550 Å and V-6370 Å).

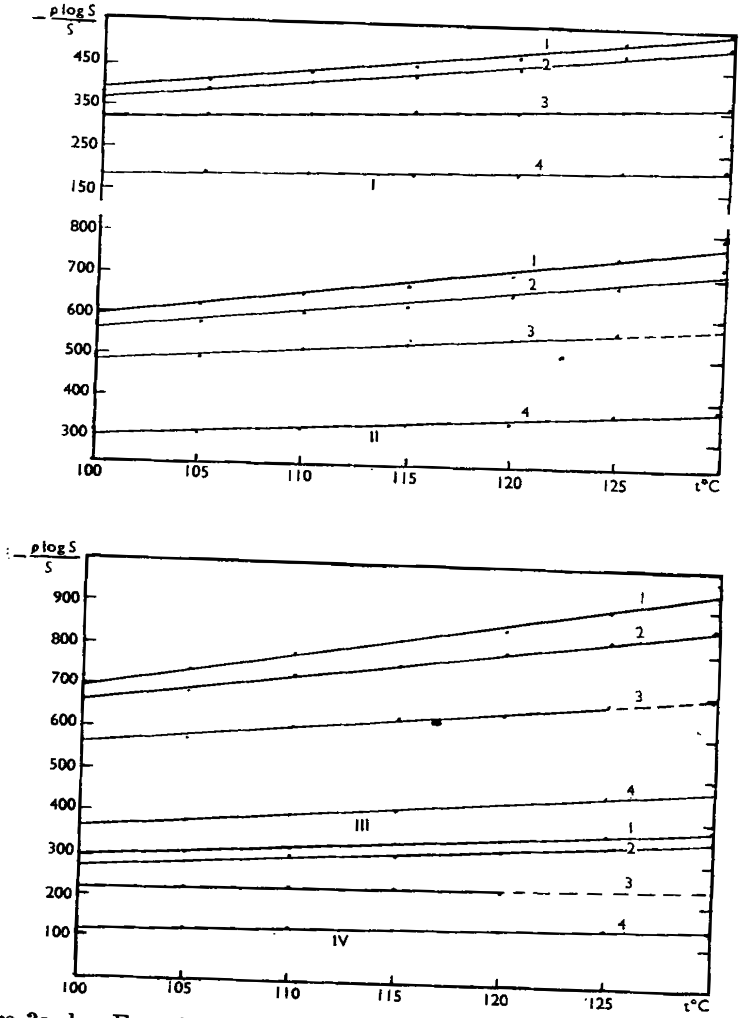

Figure 3a, b. Function $-(\rho \log S)/S$ *versus* reduced (to the pure PAA) temperature. Curves 1, 2, 3, and 4 for mixtures 1%, 1.5%, 2.5% and 5%, respectively. Families I, II, III, IV for wavelengths 5130, 4890, 4710 and 6370 Å.

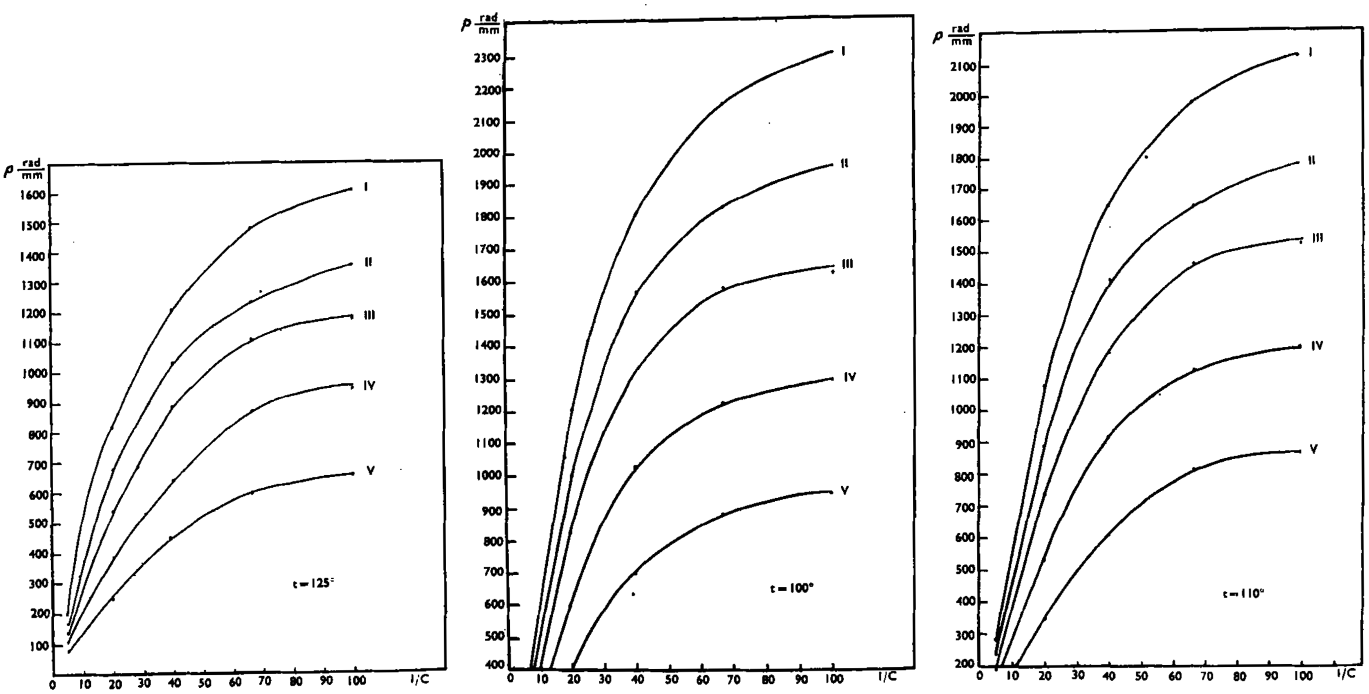

Figure 4a, b, c. Optical activity *versus* inverse concentration for different temperatures.

One can note the qualitative analogy between the influence of temperature and concentration on the optical properties of our mixtures. A decrease of both the temperature and the concentration of the propionate leads to the growth of the optical activity of the mixtures and to the displacement of inversion wavelength towards greater values. However, the change in concentration acts on these properties much more effectively.

From our results the following conclusions may be drawn:

1. The optical activity is proportional to the inverse concentration in the first approximation and for a relatively narrow region of concentrations;
2. apparently, the proportionality between the value of the pitch and the optical activity which the theory predicts is valid; hence, the dependence of the pitch on the inverse concentration has to be analogous to the dependence on the optical activity;
3. the process of formation of a new cholesteric structure at the mixing of the cholesteric substance with the nematic one, suggested by Cano and Chatelain is also apparently only approximately valid. It cannot be extended to mixtures with small concentrations. Probably the hypothesis of a simple mechanical mixing is not adequate in this case. One can suppose that for the best agreement with experiment it is necessary to consider some kind of interaction between the nematic and cholesteric structures in mixtures which would give some limiting value to the pitch.

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