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Characterization of Molecular Role in Pitch Determination in Liquid Crystal Mixtures†

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Abstract—Pitch versus composition data in a binary mixture of a cholesteric and a room-temperature nematic are used to demonstrate that molecular influence in pitch determination is more linear when credited according to weight percent than when credited according to mole %. It is also shown that the effective rotary power of cholesteryl iodide is influenced by its environment to the extent that it exhibits the chirality of the other constituent in a binary mixture.

1. Introduction

The competition between right and left handed cholesterics in pitch determination in mixtures was first reported by Friedel.(1) He observed that the chirality of a two-component mixture consisting of one right-handed and one left-handed ingredient changed from right to left as the proportion of right-handed material was increased beyond a certain point. Furthermore, there was an ingredient ratio at which the mixture exhibited the optical properties of a nematic, and, that in general, this ratio corresponded neither to equal numbers of molecules nor equal weights of ingredients. Evidently, each molecular species had a twisting influence which in general was different for different molecules. Much later, Cano showed(2,3) that in dilute mixtures of cholesterics in nematics this twisting strength was an intrinsic property of the cholesteric molecule, apparently independent from its environment. Recently, it was shown that in certain mixtures of two or more cholesterics, each cholesteric contributes to the pitch in a fashion which depends on the amount of each

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constituent and its twisting strength.(4) This twisting strength is called the effective rotary power of the molecule. The effective rotary power of a molecule is in general temperature dependent, and, if a molecular species is mesomorphic at a given temperature, then the effective rotary power at that temperature is just the inverse of the pitch. We will discuss some experiments relating to the additive law for pitch and also some observed deviations from this law.

2. Theory

The basic additive law is given by Eq. (1),

$$P = \left| \frac{100}{\sum \alpha_i \theta_i} \right| \tag{1}$$

which relates the pitch, P, of a mixture of cholesterics to the percentages and effective rotary powers of constituents. α_i is the percent of the ith ingredient in the mixture and θ_i is its effective rotary power. This relationship has been found to hold approximately true in several systems including binary and ternary mixtures of cholesteryl chloride and the fatty esters of cholesterol.(5) An example is shown in Fig. 1 where inverse pitch is shown as a

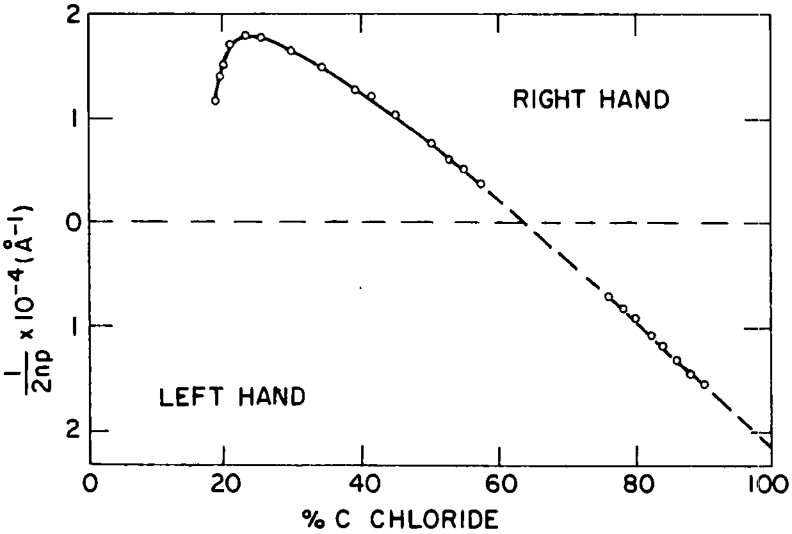

Figure 1. Relationship between pitch and composition in the cholesteryl chloride–cholesteryl nonanoate system at room temperature.

function of composition in the cholesteryl chloride–cholesteryl nonanoate system. The deviation from linearity occurring in the nonanoate rich region is attributed to the onset of the smectic mesophase. Deviations from linearity are common and have a variety of origins. This additive law is surprising in its simplicity and certainly places restrictions on models for the cholesteric structure. However, there has been an abiding ambiguity in this expression, made necessary in part by the limited number of available cholesterics. It has not been determined whether the additive law is based on mole % or weight % of ingredients. It might appear that mole % was the appropriate weighting factor and that the distinction might not be of particular significance at any rate. We will show experimental evidence that the factor which correctly assigns influence is weight % and that this fact imposes even more severe limitations on cholesteric models. To delineate the distinction between weight % and mole %, it is desirable to have a binary system in which the two constituents have considerably different molecular weights and in which mixtures are stable over a wide compositional range. This combination is very difficult to find among existing cholesterics.

To this end a binary mixture was chosen consisting of oleyl cholesteryl carbonate, molecular weight 680 and anisylidene-*p*′-*n*′-butylaniline, which we will refer to as ABUTA.(6) ABUTA is a room-temperature nematic having a molecular weight(7) of 267. This system does offer both a wide compositional range of stability and a large difference in molecular weights.

3. Experiment

Most pitch determinations were accomplished by measuring the reflectance peak of the film on a Cary Spectrometer. For normal incidence, a cholesteric film reflects, selectively, one sense of circular polarization when the wavelength is twice the index of refraction times the pitch (pitch here corresponds to one half turn of the helix). This convenient pitch-determination method was recently discussed by Baessler and Labes(8) and is implicit in work by Friedel(1) and Fergason(9) and others.(10,11) A typical reflection spectrum is shown in Fig. 2 where reflection intensity is plotted versus wavelength. The detailed line shape is a function of film-preparation technique,

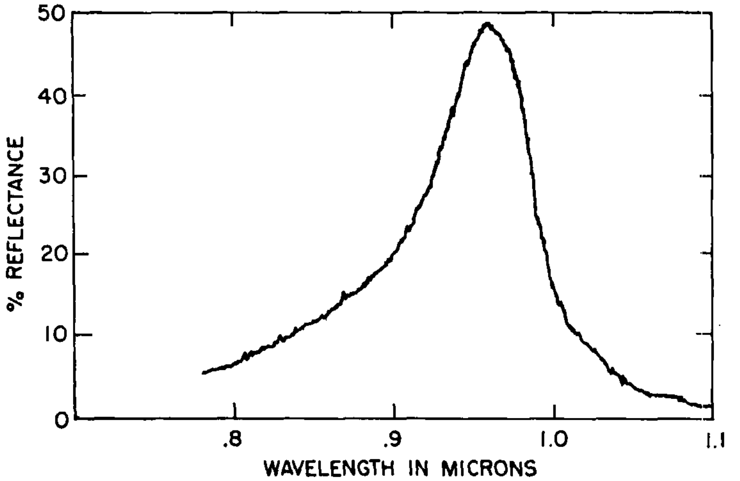

Figure 2. Reflection spectrum from a cholesteric film in Grandjean texture (70% ABUTA–30% COC).

helical-site distribution, thickness, dielectric anisotropy, etc., but this is a characteristic result.(12) It is possible to measure pitch to around 1% accuracy using this technique. Because of the fundamental absorption edge of ABUTA, it is difficult to do transmission measurements with films with reflectance maxima below 4200 Å, and, since the oleyl cholesteryl carbonate rich films fell into this regime, these were measured following a dispersive-reflection technique outlined by Fergason.(9) By measuring angle of incidence, and angle of reflection for a given wavelength, it is possible to determine pitch. Again, accuracy of around 1% is typical. When it is convenient, we now prefer the transmission technique for pitch determination.

In this particular experiment, both ingredients are mesomorphic around room temperature, and the ingredients were thoroughly mixed and films were cast directly on a glass substrate. A cover-slip displacement produced the Grandjean texture. All measurements were made in this texture, with a free surface, and at room temperature. The oleyl cholesteryl carbonate was obtained from Eastman Kodak and used as received. The ABUTA was prepared by Dr. J. B. Flannery of our laboratories. As in many experiments of this nature, purity is not a central issue and, in fact, for this particular determination, molecular weight is the only property of interest. A molecular-weight determination was performed by Galbraith Laboratories† and the weights were found to agree with expectation to within less than 2%. The experimental results for the oleyl cholesteryl carbonate-ABUTA system are shown in Fig. 3. As expected, as the sample approaches the pure nematic, the pitch approaches infinity. We have plotted in Fig. 3 the quantity $2np$ instead of p since the exact indices are not known. The n in this case is actually the average of n_0 and n_e where n_0 and n_e represent the principal indices of refraction in an ensemble of those molecules comprising the cholesteric, all aligned in the same direction.$^{(13)}$ It is possible to estimate n by combining index data$^{(14)}$ on ABUTA with an estimate of the indices of COC. The birefringence of the ABUTA decreases with increasing wavelength and the inversion wavelength increases with increasing ABUTA content, resulting in compensating influences on n. In fact, we estimate n(4000 Å) as 1.56 and n(10000 Å) as 1.59. This dispersion has a negligible effect on the arguments being presented here.

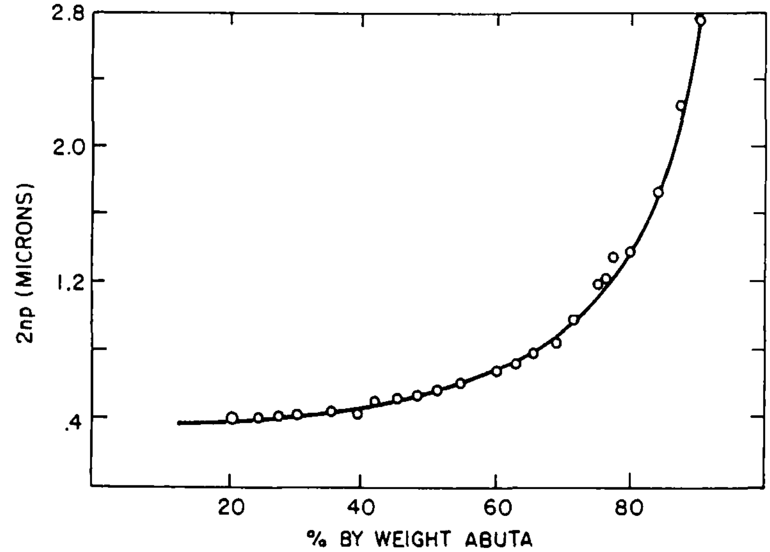

Figure 3. Pitch versus composition in a mixture of ABUTA and COC at room temperature.

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To distinguish between weight % and mole %, both are plotted versus inverse pitch in Fig. 4. We point out that there is no " correct " abscissa in this problem, and one is free to choose any parameter of interest. However, that parameter yielding the more linear behavior is clearly percent by weight. To see what this tells about the molecular organization in cholesterics, let us make some broad assumptions about the cholesteric structure. We adopt the generally accepted layer-structure model. Consider that each layer is composed of a macroscopically homogeneous distribution of type A molecules and type B molecules with a weight (or number) ratio characterized by the bulk ratio. All the molecules within a sheet lie in approximately the same direction. All sheets are identical and represent " macromolecules " in the one-dimensional crystal structure. Assume each sheet has some net rotational tendency, θ, such that when two adjacent sheets are stacked, the angle between the alignment directions of the two sheets is θ. Now assume that the effective rotary power of a species depends only on some feature of the molecule, such as a tail sticking out of the layer, or a dipole moment, etc. We assume the molecules are essentially flat (for simplicity) and have approximately the same density, so a difference in molecular weight is an implied difference in size (area). For this

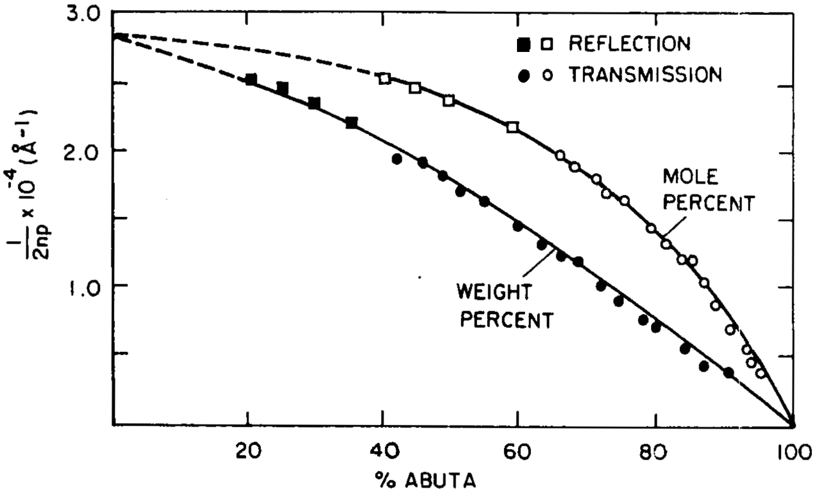

Figure 4. Comparison of weight % and mole % as a criterion for influence in binary mixtures.

model, the combination rule is simply to count features and credit only according to number and strength. This implies a linearity in mole %. If, on the other hand, the effective rotary power of a species depends on the " feature density " (for example: dipole moment/unit volume), then a linearity in weight % is expected. Our data indicate that the latter viewpoint is more correct.

Let us now proceed to a series of experiments, on a related subject, which indicates a deviation from the additive law. We have recently observed that certain molecules, in particular molecules with very small effective rotary powers, can adopt the chirality of a strong environment. The rotary strength of the molecule depends on the effective rotary power and percent by weight of the partner. An example is shown in Fig. 5 where the inverse pitch of mixtures of cholesteryl hexanoate and cholesteryl iodide are plotted versus percent cholesteryl iodide. The cholesteryl iodide has a very small rotary power as can be seen from the extrapolation to the pure material. However, in small amounts, cholesteryl iodide acts as an effective left-handed ingredient with a rotary power which is found by extrapolating the curve from the low iodide region. Evidently the effective rotary power is influenced by environment. Figure 6

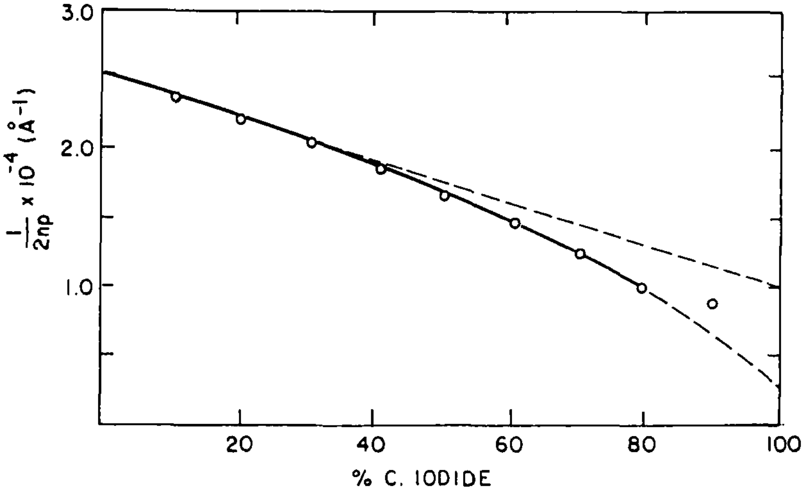

Figure 5. Behavior of cholesteryl iodide in a mixture with cholesteryl hexanoate at room temperature.

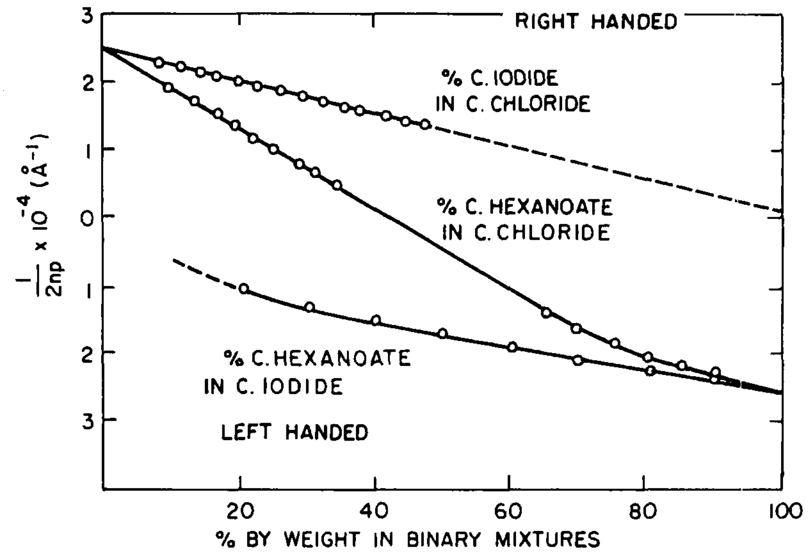

Figure 6. Behavior of cholesteryl iodide in systems of opposite chirality at room temperature.

shows the result of mixing cholesteryl iodide with a strong right-handed partner, in this case cholesteryl chloride. Here the extrapolation yields a right-handed effective rotary power for cholesteryl iodide. For comparison, the behavior in the left-handed environment is again shown. A plot of inverse pitch versus composition in a mixture of cholesteryl chloride and cholesteryl hexanoate, which are the partners of cholesteryl iodide in the other two curves, is also shown in Fig. 6. This system exhibits normal behavior, passing through a nematic point and exhibiting some curvature.

In summary, we have shown that the additive law for mixtures is most closely obeyed when ingredient influence is credited in proportion to weight and that this experimental fact implies that effective rotary power is a " feature density " property. Also, we have shown that certain molecules can exhibit either chirality, depending on environment. It is not surprising that the ERP of a molecular species is affected by its environment. We recognize that deviations from the additive law present an opportunity for gaining insight into structure since they contain additional information about interactions. The study of these deviations is an important step towards the deeper understanding of cholesterics.

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