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The Relationship Between Pitch Change and Stimulus in Cholesterics

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Abstract—An expression is derived which relates the change of pitch of a cholesteric liquid crystal to the stimulus which causes the change. The relationship is a measure of the sensitivity of the cholesteric. The expression applies to mixtures of two or more molecular species which produce a cholesteric and to any stimulus which actually or effectively changes the ratios of constituents.

The relationship between pitch and composition in mixtures of cholesterics or mixtures which produce a cholesteric has recently been developed in some detail.(1,2) It has also been shown that the response (pitch change) to a variety of stimuli can be predicted qualitatively and often quantitatively from a knowledge of this relationship.(3) The purpose of this note is to develop formally an expression which relates the change in pitch to any stimulus which changes, in general, the relative ingredient ratios and/or ingredient influences.

It has been found that for a wide variety of constituents, and over a wide compositional range, the pitch of a mixture of two or more molecular species, the combination of which exhibits the optical properties of a cholesteric, can be expressed in terms of a single intrinsic property of each species, called the effective rotary power (ERP).(2)

The ERP of a single species is, in general, temperature dependent and if the species is mesomorphic at some given temperature, then the ERP at that temperature is just the inverse of the inversion wavelength, $\lambda_0 = 2np$, where n is the index of refraction. The relationship between pitch, p, and composition, for a mixture of N

molecular species, is given below:

$$p = \left| \frac{1}{\sum_{i=1}^{N} \alpha_i \theta_i} \right| \tag{1}$$

where α_i is the percent by weight of the ith ingredient and θ_i is its ERP.

Equation (1) has been written using absolute values on the right because, conventionally, pitch is an intrinsically positive quantity. In fact, pitch is a pseudoscalar consisting of a sense or chirality and a magnitude. The chirality changes sign under an improper rotation.

It is convenient, however, to consider that the symbol, p, represents the magnitude of the pitch only, since then statements such as $\partial p/\partial T < 0$ ($\mathrm{d}T$ is a change in temp.) mean that the sample in question shifts towards the blue with heat whether it is a left-handed or right-handed cholesteric. An alternative treatment would allow p to process an algebraic sign, for example, positive for right-handed films and negative for left-handed films. But, in this case, $\partial p/\partial T < 0$ would mean either that a right-handed film was shifting toward blue with heat or a left-handed film was shifting toward red with heat.

We suggest that a more attractive representation is to rewrite Eq. (1) as follows:

$$p = \frac{\operatorname{sgn}\left(\sum_{i=1}^{N} \alpha_i \theta_i\right)}{\sum_{i=1}^{N} \alpha_i \theta_i} \tag{2}$$

where $\operatorname{sgn} \sum_{i=1}^{N} \alpha_i \theta_i$ is the algebraic sign of $\sum_{i=1}^{N} \alpha_i \theta_i$. That is:

$$\begin{aligned} \sum_{i=1}^{N} \alpha_i \theta_i > 0 &\rightleftarrows \operatorname{sgn} \sum_{i=1}^{N} \alpha_i \theta_i = 1 \\ \sum_{i=1}^{N} \alpha_i \theta_i < 0 &\rightleftarrows \operatorname{sgn} \sum_{i=1}^{N} \alpha_i \theta_i = -1 \end{aligned} \tag{3}$$

This guarantees that p is always positive and allows for the correct algebraic assignment in any derivative calculation.

The chirality of the film is manifested by sgn $\sum \alpha_i \theta_i$ and we suggest that

$$\begin{aligned} &\operatorname{sgn} \sum_{i=1}^{N} \alpha_i \theta_i = 1 \quad \rightleftarrows \text{Right-handed} \\ &\operatorname{sgn} \sum_{i=1}^{N} \alpha_i \theta_i = -1 \rightleftarrows \text{Left-handed} \end{aligned} \tag{4}$$

Of course, this convention requires that right-handed ingredients be assigned positive ERP'S, etc.

It is now possible to calculate the general pitch change in a mixture of N different molecular species resulting from a differential energy input, dE, starting from Eq. (2). Evidently:

$$\frac{\mathrm{d}p}{\mathrm{d}E} = \sum_{i=1}^{N} \left(\frac{\partial p}{\partial \alpha_i} \frac{\mathrm{d}\alpha_i}{\mathrm{d}E} + \frac{\partial p}{\partial \theta_i} \frac{\mathrm{d}\theta_i}{\mathrm{d}E} \right). \tag{5}$$

This takes into account the possibility that: 1. The input may change the individual ERP'S, for example, temperature; 2. The input may change the chemical composition, for example, exposure to ultraviolet light;(4) 3. a combination of (1) and (2). Since all the α_i's are not independent variables, there is a constraint on Eq. (5) given by

$$\sum_{i=1}^{N} \alpha_i = 1 \tag{6}$$

It is convenient to eliminate one of the α_i's from Eq. (5) by writing Eq. (6) as

$$\alpha_k = 1 - \sum_{i=1}^{N}{}' \alpha_i \tag{7}$$

where α_k is any arbitrary species and $\sum_{i=1}^{N}{}'$ is a deleted sum which omits the term $i = k$. Then Eq. (2) becomes

$$p = \frac{\operatorname{sgn}\left[\sum_{i=1}^{N}{}' \alpha_i \theta_i + \left(1 - \sum_{i=1}^{N}{}' \alpha_i\right) \theta_k \right]}{\sum_{i=1}^{N}{}' \alpha_i \theta_i + \left(1 - \sum_{i=1}^{N}{}' \alpha_i\right) \theta_k} \tag{8}$$

For notational convenience we introduce

$$\sum \equiv \sum_{i=1}^{N}{}' \alpha_i \theta_i + \left(1 - \sum_{i=1}^{N}{}' \alpha_i\right) \theta_k \tag{9}$$

and,

$$S \equiv \operatorname{sgn} \sum .$$

So,

$$p = \frac{S}{\sum} . \tag{10}$$

It is now desirable to calculate the individual $\partial p/\partial \alpha_i$ and $\partial p/\partial \theta_i$ which will then be substituted into Eq. (5). Evidently,

$$\frac{\partial p}{\partial \alpha_i} = \frac{\partial S/\partial \alpha_i}{\sum} + \frac{S(\theta_i - \theta_k)}{-(\sum)^2} \tag{11}$$

and, similarly,

$$\frac{\partial p}{\partial \theta_i} = \frac{\partial S/\partial \theta_i}{\sum} + \frac{S\alpha_i}{-(\sum)^2}, \quad i \neq k,$$

and,

$$\frac{\partial p}{\partial \theta_k} = \frac{S\left(1 - \sum_{i=1}^{N}{}' \alpha_i\right)}{-(\sum)^2} \tag{12}$$

Combining Eqs. (10), (11), and (12) in Eq. (5) gives:

$$\frac{\mathrm{d}p}{\mathrm{d}E} = \sum_{i=1}^{N} \left[\frac{1}{\sum\limits_{i=1}^{N}} \left(\frac{\partial}{\partial \alpha_i} + \frac{\partial}{\partial \theta_i} \right) S \right]$$

$$- Sp^2 \left\{ \left[\sum_{i=1}^{N}{}' (\theta_i - \theta_k) \frac{\mathrm{d}\alpha_i}{\mathrm{d}E} + \alpha_i \frac{\mathrm{d}\theta_i}{\mathrm{d}E} \right] + \frac{\mathrm{d}\theta_k}{\mathrm{d}E} 1 - \sum_{i=1}^{N}{}' \alpha_i \right\} \tag{13}$$

Turning attention to the first term

$$\frac{\partial}{\partial \alpha_i} S = \frac{\partial}{\partial \lambda_i} S = 0$$

except when $\sum$ itself vanishes, so we represent this term as $\delta \sum$ where δ is theDirac delta function used in this case to denote singularities in $\mathrm{d}p/\mathrm{d}E$. It is interesting to investigate those combinations of α_i which, for a given system, result in $\sum = 0$. It is convenient to introduce an N-dimensional orthogonal coordinate system to describe a system comprised of N molecular species. A given mixture is represented by a point in this space, the coordinates of which are proportional to the α_i. For example, in a three-component mixture, the locus of points satisfying $\sum_{i=1}^{3} \alpha_i = 1$ is a plane in the first octant $(\alpha_1, \alpha_2, \alpha_3 \geqslant 0)$. $\sum_{i=1}^{3} \alpha_i \theta_i = 0$ is also a plane passing through the origin which may or may not have points in common (intersect) $\sum_{i=1}^{3} \alpha_i = 1$. In general, then, the intersection of the hyperplane $\sum_{i=1}^{N} \alpha_i = 1$ and the hyperplane $\sum_{i=1}^{N} \alpha_i \theta_i = 0$ in the first hyperquadrant $(\alpha_i \geqslant 0)$ is the locus of points for which $\sum = 0$.

The general expression relating pitch change to stimulus is given by:

$$\frac{\mathrm{d}p}{\mathrm{d}E} = \delta(\textstyle\sum) - Sp^2 \left\{ \left[\sum_{i=1}^{N}{}' (\theta_i - \theta_k) \frac{\mathrm{d}\alpha_i}{\mathrm{d}E} + \alpha_i \frac{\mathrm{d}\theta_i}{\mathrm{d}E} \right] + \frac{\mathrm{d}\theta_k}{\mathrm{d}E} \left(1 - \sum_{i=1}^{N}{}' \alpha_i \right) \right\}. \quad (14)$$

The above development is not limited to systems described by Eq. (1). Many systems fail to obey the additive law in certain compositional regions (i.e., Ref. 3). As long as the functional dependence on composition is known, similar arguments can be applied. For example, the ERP of an ingredient may be a function of its environment (i.e., depend on other ERP's, concentrations, etc.) or may be represented as such, in which case the derivatives will simply be more complicated.

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