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Pitch Dependence on Composition in Mixtures of Liquid Crystals

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The linear additive law for pitch dependence in binary mixtures of cholesterics (or combinations of ingredients producing cholesterics) is extended to include first order interactive effects. The resulting expression is shown to effectively treat an apparently widely diverse collection of experimental data. The knowledge of the functional form of any given system is of value in predicting pitch sensitivity to heat, vapor, etc.

I INTRODUCTION

The first insight into the relationship between pitch and constituent properties in cholesteric mixtures was provided by Friedel[1] in 1922. He observed that in binary mixtures consisting of one intrinsically left-handed (LH) species and one intrinsically right-handed (RH) species there was one ingredient ratio at which these competing effects essentially canceled and the pitch approached infinity. Mixtures richer in LH material exhibited LH behavior, and mixtures richer in RH material exhibited RH behavior; in both cases, the pitch decreased as the single component was approached. A special case of this general trend was treated quantitatively by Cano[2,3,4] who demonstrated that in certain mixtures of cholesterics and nematics, the nematic played a passive role, indicated by the fact that the reciprocal pitch varied linearly with percent cholesteric.

The case of two cholesterics was first treated quantitatively[5] in 1969 and through the introduction of the idea of effective rotary power (ERP), extended to three- and four-component systems.[6] Simply stated, many systems behave as if each constituent molecule has an intrinsic rotational strength or "effective rotary power" which is independent of its concentration, the nature of the other molecular species in the mixture, etc. Many systems can be closely described by this model, however, several show deviations ranging from minor to severe.

A typical example is the behavior of cholesteryl iodide in binary mixtures.[7] This molecule is influenced by the chirality of its partner and actually changes sign depending on environment. A striking example of large deviation from the linear additive approach involves a mixture of a nematic and a cholesteric.[8] It is the purpose of this communication to outline a more general approach to this problem and, in particular, to suggest a three-parameter expression which closely describes all the above data. The basic argument involves an extension of the ERP viewpoint to include induced effects.

II THEORY

The cholesteric structure is characterized by a helical arrangement, and it is necessary to specify both pitch and chirality for a complete description (pitch will be defined as the distance along the screw axis corresponding to a 180° rotation). It is possible to express this quantity mathematically in the form of a pseudoscalar which can be operated on[9]; however, this viewpoint is too formal for the present argument and obscures the point. We will speak in terms of a scalar pitch, p, and a sense which will simply be stated. Although pitch is the parameter characterizing the experimentally observed interactions with light, it is also convenient to introduce a "specific rotation", θ, which is defined as $(2np)^{-1}$, where n is the appropriate index of refraction. Of course, θ has dimensions of inverse length. This is very similar to the reciprocal lattice vector approach in solids, except for the complication of algebraic sign. The quantity θ is more convenient to deal with mathematically since it passes through zero continuously at the point on a compositional diagram where the pitch has a singularity. The linear additive law for a binary system is just

$$\theta = \alpha\theta_A + (1 - \alpha)\theta_B, \tag{1}$$

where α is the weight fraction[7] of ingredient A and θ_A is its ERP, etc. We now propose to modify this expression by taking into account the fact that the presence of A may influence the role of B and conversely, i.e., type-A molecules may induce a behavior or tendency in type-B molecules. If k_A^B is a measure of the modification of the effective rotary power of A resulting from the presence of B, then Eq. 1 becomes

$$\theta = \alpha[\theta_A + (1 - \alpha)k_A^B] + (1 - \alpha)[\theta_B + \alpha k_B^A] \dots \tag{2}$$

Since it is not possible to experimentally isolate the k_A^B and k_B^A, Eq. 2 can be written

$$\theta = \alpha\theta_A + (1 - \alpha)\theta_B + \alpha(1 - \alpha)k(A, B)\ldots \tag{3}$$

This is easily extended to an N component system according to

$$\theta = \sum_{i=1}^{N}\left[\alpha_i\theta_i + \sum_{j=i+1}^{N}\alpha_i\alpha_j k(i, j)\right]\ldots \tag{4}$$

Subject to the constraint

$$\sum_{i=1}^{N}\alpha_i = 1 \tag{5}$$

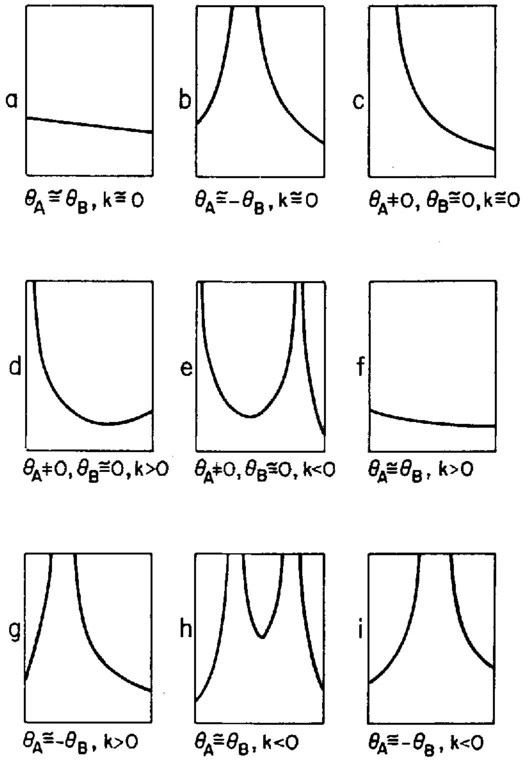
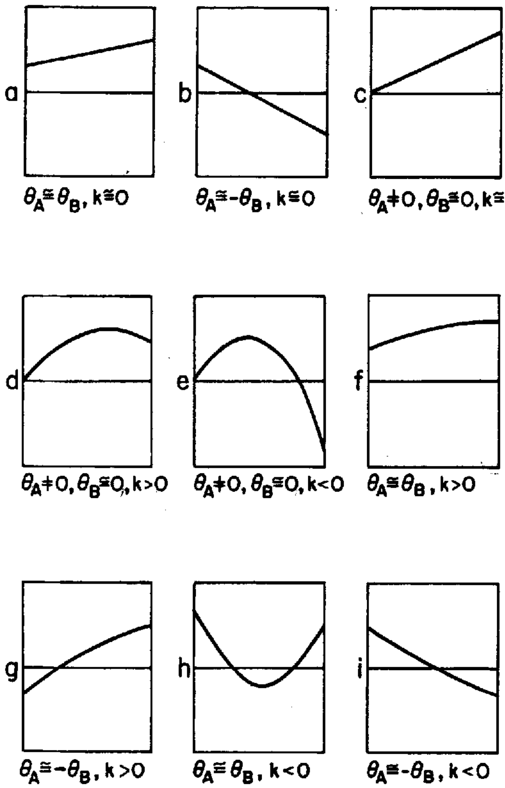


FIGURE 1 Pitch versus composition in binary systems for nine different cases contained in Eq. 2. Pitch is plotted vertically and α horizontally with α varying from 0 to 1. Both axes are linear.

The specific form of Eq. 3 is not unique regarding the grouping of constants. It is simply a three-parameter function quadratic in α. Figure 1 is a schematic representation of nine different cases, all contained in Eq. 3. An example of each case has been reported in the literature. Pitch is plotted on the vertical axis and the fraction of B on the horizontal axis. The corresponding behavior of θ is shown in Figure 2.



$\theta_A \cong \theta_B, k \cong 0$ $\theta_A \cong -\theta_B, k \cong 0$ $\theta_A \neq 0, \theta_B \cong 0, k \cong 0$

$\theta_A \neq 0, \theta_B \cong 0, k > 0$ $\theta_A \neq 0, \theta_B \cong 0, k < 0$ $\theta_A \cong \theta_B, k > 0$

$\theta_A \cong -\theta_B, k > 0$ $\theta_A \cong \theta_B, k < 0$ $\theta_A \cong -\theta_B, k < 0$

FIGURE 2 Specific rotation for the nine systems shown in Figure 1. θ is plotted vertically and α horizontally.

We wish to observe that it is surprising that Eq. 3 describes so many results very closely without recourse to higher order interactions (more parameters). In the next section, we will analyze selected pitch vs. composition data. All percentages are by weight.[7]

III COMPARISON WITH EXISTING DATA

To our knowledge, all of the existing pitch vs. composition data in the literature can be fitted reasonably well to Eq. 3 except near critical points in compositional regions such as phase transformations, etc. It is the purpose of this section to show that several systems of apparently widely varying behavior are all cases treated by Eq. 3. For binary systems, $k(A, B)$ will be written as k. The nine systems treated provide one example for each of the nine possible combinations of θ_A, θ_B and k for the case when either or both θ_A and θ_B are nonzero. There are three other combinations which occur when $\theta_A = \theta_B = 0$ which are $k > 0$, $k < 0$ and $k \cong 0$. Examples of these cases are not presented.

Case A: $\theta_A \cong \theta_B, k \cong 0$

A good example of this situation is found in the cholesteryl chloride-cholesteryl bromide system.[6]

Case B: $\theta_A \cong -\theta_B, k \cong 0$

A system which is stable over almost the entire compositional range and exhibits this behavior very nicely is a binary mixture of oleyl cholesteryl carbonate and cholesteryl chloride.[10] Another example is the cholesteryl chloride-cholesteryl nonanoate system.[6] However, in the cholesteryl nonanoate-rich region, the pitch vs. composition behavior is violent and has been associated with a tendency of the mixture to be smectic.

Case C: $\theta_A \neq 0, \theta_B \cong 0, k \cong 0$

Here, one of the ingredients has a helical tendency and the other is passive. An excellent example is found among the exhaustive data presented in Cano's thesis[3] which, undoubtedly, is the most complete collection of information of that nature available. The binary system is comprised of a mixture of active and racemic *p*-amyl-cyano-benzalaminocinnamate. The racemic component, is of course, the passive agent.

Case D: $\theta_A \neq 0, \theta_B \cong 0, k > 0$

The argument in this case is only qualitative since it is based on data taken at different temperatures.[11] The system consists of cholesteryl propionate (CP) and methoxy-benzylidene *p*-aminophenyl acetate (MBA) which exhibits a minimum pitch at around 80% CP. All data were taken at 8°C below the cholesteric-isotropic transition point which varies with concentration. Judging from the clearing points of the two species, temperature increased slightly with increasing CP content, which in the absence of any interaction ($k = 0$) would have caused a curvature opposite to that reported (i.e. $\partial^2\theta/\partial\alpha^2 > 0$) where $\alpha = \%$ by weight MBA. If, on the other hand, temperature were decreasing with increasing α, the maximum could be explained simply in terms of a decreasing MBA ERP.

Case E: $\theta_A \neq 0, \theta_B \cong 0, k < 0$

This situation is contained in data from Saeva and Wysocki[8] comprising mixtures of *N*-(*p*-methoxybenzylidene)-*p*-butylaniline (MBBA) and cholesteryl chloride (CC). As in Case *D*, one component is inert and the other induces an ERP in its partner. However, here the induced ERP is opposite in sign from the active species. It was this data that triggered our interest in this problem. In fact, if an ERP is simply calculated for the nematic for each compositional value, it is found that this ERP is linearly proportional to the amount of cholesteric present, suggesting a relationship of the form of Eq. 3. A computer fit is shown in Table I.

TABLE I

α = percent by weight of MBBA in a mixture with CC.

α	θ(Calculated) × 10^{-4}Å^{-1}	θ(Observed) × 10^{-4}Å^{-1}
0.15	−0.51	−0.55
0.20	−0.67	−0.68
0.25	−0.80	−0.79
0.30	−0.88	−0.85
0.35	−0.92	−0.88
0.40	−0.92	−0.89
0.45	−0.88	−0.86
0.50	−0.79	−0.80
0.55	−0.67	−0.70
0.60	−0.50	−0.58
0.80	+0.58	0.59
0.85	+0.95	1.03
0.90	+1.37	1.33

$\theta_A = +2.32 \quad \theta_B = +0.237 \quad k = -8.30$

Case F: $\theta_A \cong \theta_B, k > 0$

An excellent example of this is found in Ref. 5 in the cholesteryl formate (CF), cholesteryl nonanoate (CN) system. The results of a computer fit are shown in Table II.

TABLE II

α = percent by weight of CN in a mixture with CF.

α	θ(Calculated) × 10^{-4}Å^{-1}	θ(Observed) × 10^{-4}Å^{-1}
0.30	+2.52	+2.52
0.35	+2.46	+2.46
0.40	+2.38	+2.38
0.45	+2.29	+2.29
0.50	+2.19	+2.19
0.55	+2.08	+2.08
0.60	+1.95	+1.95
0.65	+1.82	+1.82
0.70	+1.67	+1.68
0.75	+1.51	+1.51
0.80	+1.34	+1.33
0.85	+1.15	+1.15

$\theta_A = 0.52 \quad \theta_B = 2.66 \quad k = 2.43$

Case G: $\theta_A \cong -\theta_B, k > 0$

The cholesteryl oleyl carbonate (COC), $\Delta^{5,7}$ cholesteryl benzoate (CB) system reported by Leder[12] shows this effect. The results of a computer fit are shown in Table III.

TABLE III

α = percent by weight of CB in COC.

α	θ(Calculated) × 10^{-4}Å^{-1}	θ(Observed) × 10^{-4}Å^{-1}
0.0	−2.74	−2.79
0.1	−1.60	−1.59
0.2	−0.57	−0.50
0.3	+0.38	+0.40
0.4	+1.22	+1.20
0.5	+1.97	+1.99
0.6	+2.62	+2.59
0.7	+3.17	+3.18
0.8	+3.63	+3.59
0.9	+3.99	+3.99
1.0	+4.25	+4.29

$\theta_A = +4.24 \quad \theta_B = -2.74 \quad k = +4.87$

Case H: $\theta_A \cong \theta_B, k < 0$

A recent paper by Stegemeyer and Finkelmann[13] discloses a binary system exhibiting these properties. The two constituents, cholesteryl-2-(ethoxy ethoxy) ethyl carbonate (CEEC) and amyl-*p*-(4-cyanobenzylidene amino)—cinnamate (CBAC) are both right-handed cholesterics. The pitch versus composition curve is remarkable, showing two singularities and a region in the center within which the mixture is left-handed. As in case *D*, this was not a constant temperature experiment and therefore cannot logically be fit to Eq. 3. However, a qualitative argument can be made that this system is an example of case *H*. Since no single cholesteric is known to change pitch sense with temperature it is plausible to assume that at all temperatures involved both the CEEC and CBAC exhibit right handed behavior by themselves. Consequently the observed left handed behavior implies a $k < 0$.

Case I: $\theta_A \cong -\theta_B, k < 0$

Binary mixtures of oleyl cholesteryl carbonate and doristeryl esters exhibit this behavior.[12] Doristerol is a cholesterol-like steroid having its double bond at the 8–14 position and has been called α cholestanol, $\Delta^{8(14)}$-cholestanol, etc. A detailed discussion is found in Ref. 12.

IV CONCLUSION

By assuming only first order interactions, it has been possible to derive an equation which essentially treats all existing pitch vs. composition data. It was intended to develop an empirical expression which could be applied to a variety of systems. The detailed interactions are not considered and we do not wish to imply that significant structural conclusions can be drawn. There is considerable present interest in thermography, vapor detection and so forth, and it is hoped that Eq. 3 will be a useful working expression for predicting system response.

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