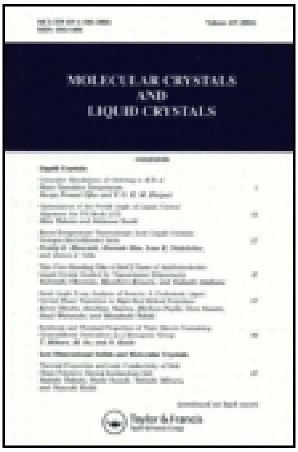

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On the Improvement of the Optical Properties of the Dichroic Dyes and Liquid Crystal Mixtures. A Model Studies

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On the Improvement of the Optical Properties of the Dichroic Dyes and Liquid Crystal Mixtures. A Model Studies

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Guest-host type mixtures of a liquid crystal and dichroic dyes are theoretically analyzed by means of the Flory–Ronca lattice theory.

The results are compared with experimental data. The influence of the temperature, molecular soft- and steric interactions, dyes (guest) ratio and presence of different dopants on the optical properties of the mixture is also analyzed.

Keywords: dichroic dyes, guest-host mixtures, Flory–Ronca theory.

1. INTRODUCTION

The properties of guest-host mixtures such as liquid crystal-dichroic dyes are very interesting from the molecular interaction point of view and also because of their possible applications. Recently developed guest-host type LC cells possess very good optical properties, i.e. brightness and contrast ratio. The cell is filled with the homogeneously ordered LC and doped with a small amount of dichroic dye molecules (typically 0.7 w.t.%, Figure 1). Due to the guest-host effect, the dye molecules reorient in the same way as the LC matrix and because of the dye's dichroism, the color is obtained.[1] The most important optical properties of such a cell are related to the dichroic ratio of the dyes.[2]

Since a value of the dichroic ratio is strictly connected with the orientational order of the dyes, a good understanding of the molecular interactions in guest-host mixtures is of great importance. In this paper we summarize theoretical results concerning the possibility of improving optical properties of the considered substances. We base our approach on the well established Flory–Ronca[3] model, which deals very well with the mixtures of rod-like particles. It also determines relations between the molecular parameters of the mixed substances and the macroscopic performance of the mixture.

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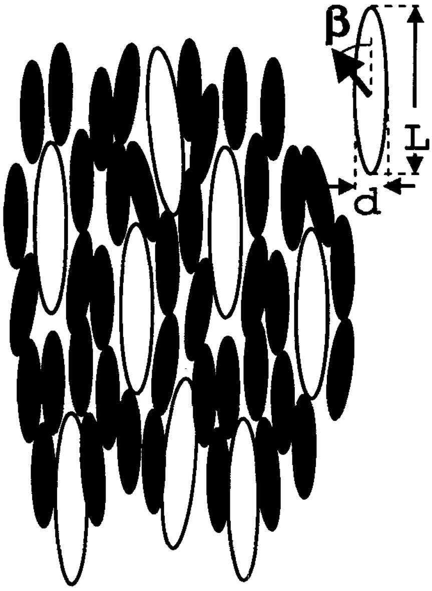

FIGURE 1 Example of the considered mixtures. Black molecules correspond to the liquid crystal (LC) whereas the white ones show the dichroic dyes, β denotes the transition moment angle.[2]

Generally we study two types of interactions:[1] the steric interactions, for which the Flory approach, in case of higher densities, is more precise than "the excluded volume" approximation and,[2] the soft, nematic interactions, taken into account in usual Maier–Saupe form.[3]

First we verify the model with the experimental results,[2] then study the dichroic ratio of the mixture as a function of arbitrarily changed microscopic parameters.

2. THEORY

2.1. The Flory–Ronca Model. Steric Interactions

First we consider the cubic lattice filling space. We start a model construction from the ideally oriented nematic phase. We assume that the nematic director is parallel to the Z axis of the lattice.

Next we assume that the molecule diameter is equal to the size of lattice cell, d, and that its length is L. In this case the molecule is defined as a sequence of $l = L/d$ occupied cells, parallel to Z.

The molecule is distorted from the ideal orientation we described in Figure 2. According to Figure 2, we introduce the Flory disorder parameter, m, as follows:

$$m - 1 = m_x + m_y = (l - 1)\sin\psi(|\cos\phi| + |\sin\phi|) \tag{1}$$

where ψ is the angle between the molecule long axis and the director, and ϕ denotes the angle between the molecule projection on the X, Y plane and the X axis.

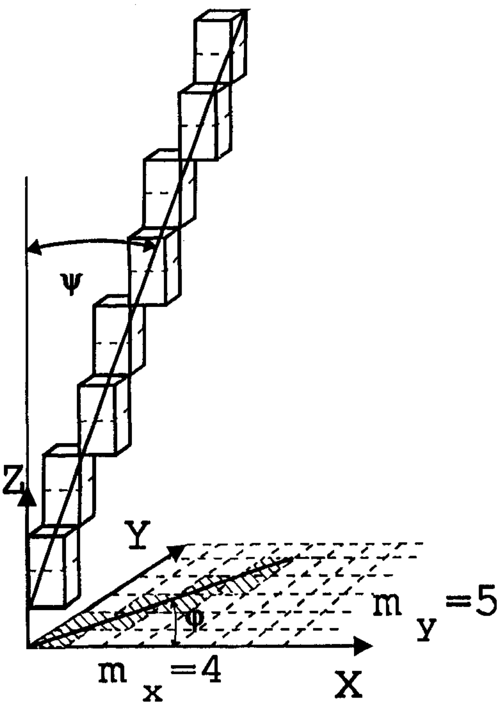

FIGURE 2 The model molecule of $L/d = l$ and disorder parameter $m = m_x + m_y$.

After averaging Eq. (1) over ϕ:

$$m - 1 = \frac{4}{\pi}(l - 1)\sin\psi, \tag{2}$$

In the model we apply the recently improved definition of the m parameter.[6,7] This modification is required because the L/d of the molecules considered is rather small in comparison to the polymer molecules for which the model was developed. Due to that, the values of m and l are small and the simplifications $(m - 1) \approx m$, $(l - 1) \approx l$ are no longer valid.[6,7]

A further step is the construction of the partition function, expressed in terms of m and l. Assume that the lattice consists of n_0 cells and we have n_α molecules of length l_α, where α denotes either LC molecules or the dyes. The average values for the system can be written as follows:[4,5]

$$n_p = \sum_\alpha n_\alpha, \quad n_0 = n_s + \sum_\alpha l_\alpha n_\alpha,$$

$$\bar{l} = \sum_\alpha l_\alpha\left(\frac{n_\alpha}{n_p}\right), \quad \bar{m}_\alpha = \sum_{m_\alpha} m_\alpha\left(\frac{n_{m_\alpha}}{n_\alpha}\right),$$

$$\bar{m}_p = \sum_\alpha \bar{m}_\alpha\left(\frac{n_\alpha}{n_p}\right), \quad v_p = \bar{l} n_p / n_o, \tag{3}$$

where n_{m_α} is the number of α type molecules with the disorder parameter m_α, n_p is the total number of molecules, n_s the number of empty cells on the lattice, $\bar{l}$ average length, $\bar{m}_p$ average disorder parameter for the system and v_p denotes the volume density of the molecules.

For further calculations we use the Gibbs potential of the system, developed by Warner and Flory:[5]

$$G/kT = -\ln(Z_o) - \ln(Z_c) = -[n_o - n_p(\bar{l} - \bar{m}_p)]\ln[n_o - n_p(\bar{l} - \bar{m}_p)] + n_s \ln(n_s) + \sum_\alpha n_\alpha \ln(n_\alpha) + n_p \bar{m}_p - n_p(1 - \bar{m}_p)\ln(n_o) - \sum_{\alpha, m_\alpha} n_{m_\alpha} \ln\left(\frac{\sigma \omega_{m_\alpha} n_\alpha e}{n_{m_\alpha}}\right) \tag{4}$$

where ω_{m_α} is the statistical weight connected with orientations[3,5] and σ an arbitrary constant.[3]

The considered mixture is always in a pure nematic phase so it is not necessary to examine the chemical potentials as in the original model.[4,5]

The equilibrium state is given by minimizing this function (Eq. (4)), i.e. by equating the functional derivative $\delta G/\delta n_{m_\alpha} = 0$. The equilibrium orientational distribution function is given by:

$$\frac{n_{m_\alpha}}{n_\alpha} = (\omega_{m_\alpha}/f_1^\alpha)\exp(-a m_\alpha) \tag{5}$$

where:

$$f_1^\alpha = \sum_{m_\alpha} \omega_{m_\alpha} \exp(-a m_\alpha) \tag{6}$$

and:

$$a = -\ln(1 - v_p(1 - \bar{m}_p/\bar{l})) \tag{7}$$

Applying Eq. (2) we can write:[5]

$$f_n^\alpha = \int_0^{\pi/2} \sin^n \psi \exp[-(l_\alpha - 1)(\tfrac{4}{\pi} a \sin\psi)]\, d\psi \tag{8}$$

Combining Eqs. (2, 5, 8) results in:

$$\bar{m}_\alpha - 1 = \frac{4(l-1) f_2^\alpha}{\pi f_1^\alpha} \tag{9}$$

The order parameter, defined as follows:

$$s_p = \sum_\alpha s_\alpha (n_\alpha l_\alpha / v_p) \tag{10}$$

with:

$$s_\alpha = (3\langle \cos^2 \psi_\alpha \rangle - 1)/2 \tag{11}$$

will be given by a similar self-consistent equation:[5]

$$s_\alpha = 1 - \frac{3f_3^\alpha}{2f_1^\alpha} \tag{12}$$

The solutions of Eq. (9) and Eq. (12) provide the equilibrium parameters m_α and s_α for the nematic phase of the considered guest-host mixture.

2.2. The Soft Interactions

In the model, following the idea of Flory,[3] we consider the interaction of each segment of the molecule with its surroundings. Since the interactions are proportional to $1/r^6$ we limit ourselves to the first neighboring range. In the mean field approximation, the potential of interactions of one cell in the molecule considered $E = E(\psi_\alpha, \eta_\alpha)$ has a form:[3]

$$E(\psi_\alpha, \eta_\alpha) = -\eta_\alpha v_p s_p (1 - 3/2 \sin^2 \psi_\alpha) \tag{13}$$

where η_α is the unit strength of the interactions for LC (α = LC) and dyes (α = Dye) with the surroundings. To obtain the interaction of the whole molecule within the mean-field limit, we sum the contributions from all cells in the molecule. This results in the proportionality of the potential to the specie's length (l_α). This assumption is based on the fact that the experimentally studied liquid crystals and dyes differ, not only by the length of the methyl chains but also by the number of benzene rings or similar parts which undergo the soft, nematic interactions. Originally the model was developed for the polymer molecules, where the periodicity of the structure was self-evident. When compared to the experimental data, however, this proportionality approach seems more reasonable than the usual center of mass to center of mass approach.[2] We will comment on this fact in the last section.

The total change of the orientation dependent energy of the system is obtained by summing Eq. (13) over all pairs of interacting cells:

$$\Delta G = -\frac{1}{2}\frac{v_p s_p^2}{k_B T}(n_{\mathrm{Dye}} l_{\mathrm{Dye}} \eta_{\mathrm{Dye}} + n_{\mathrm{LC}} l_{\mathrm{LC}} \eta_{\mathrm{LC}}), \tag{14}$$

and due to the Eq. (13) the change of the equilibrium orientational function will be:[5]

$$f_n^\alpha = \int_0^{\pi/2} \sin^n \psi \exp\left[-(l_\alpha - 1)\left(\frac{4}{\pi}a + \frac{3 v_p s_p \eta_\alpha}{2 k_B T} \sin\psi\right)\sin\psi\right] d\psi \tag{15}$$

The equilibrium conditions of the system are still given by Equations (9, 12) but includes the changes of Eqs. (14, 15).

3. NUMERICAL RESULTS AND COMPARISON WITH EXPERIMENT

All important optical properties of the LC-dichroic dyes mixtures are directly related to the dichroic ratio, DR, of the dyes. The dichroic ratio is easily evaluated from the order parameter, given by the equilibrium conditions in Eq. (12). It is useful to redefine the order parameter by introducing D_{Dye}, $D_{\mathrm{Dye}} = \frac{2S_{\mathrm{Dye}}+1}{1-S_{\mathrm{Dye}}}$. The D_{Dye} can be expressed as a function of the dichroic ratio, DR:

$$D_{\mathrm{Dye}} = \frac{2DR - DR\sin^2\beta - \sin^2\beta}{2 - DR\sin^2\beta - \sin^2\beta}, \tag{16}$$

where β is the angle between the dye long axis and the optically active part of the molecule (transition moment, Figure 1).[1,2] In our case $\beta = 0$ so we have a simple relation: $D_{\mathrm{Dye}} = \mathrm{DR}$.

In order to verify the model we compare the numerical results with the experimental data. First we consider the LC-GR41 and AZO-type dye system.[2] Because of the purely thermotropic behavior of the mixtures we set the volume concentration v_p, to 0.99, although in further calculations we also study the influence of this value on the model results.

Within the model there are four important parameters: steric, $L/d_{\mathrm{LC}} = l_{\mathrm{LC}}$ (the length to diameter ratio of the host liquid crystal), $L/d_{\mathrm{Dye}} = l_{\mathrm{Dye}}$ (the same for the guest dye molecules) and two parameters related to the temperature, $\eta_{\mathrm{Dye}}/k_B T$, $\eta_{\mathrm{LC}}/k_B T$. For numerical calculations we use redefined constants:

$$T^* = \eta_{\mathrm{LC}}/\mathrm{k}_B\mathrm{T},\ \eta = \eta_{\mathrm{Dye}}/\eta_{LC} \tag{17}$$

T^* scales the soft interactions of the LC matrix and η denotes ratio of the soft interactions for the dyes and LC.

The scaling procedure for the numerical data is as follows: the steric coefficients were obtained from the structures of the molecules.[2] In the case of GR41 LC, a mixture of many compounds, we average the L/d_{LC} over the system which gives the value of 2.98.[2] The value of η_{LC} is found by comparing the model ($T_C^* = \eta_{\mathrm{LC}}/k_B T_C$) and real clearing point temperature of the LC ($T_C = 335$ K). Next we input the measurement temperature (299 K) into the Eq. (17) and obtain $T^* = 1.43$. The approximated values of η for two types of dyes are taken from the plots of [2], then we look for the best fit, changing values of η only. The results are presented on Figure 3.

Since the molecular structures of the GR41 mixture and the 5CB hosts are similar, for further calculations we use the fitted values of η from Figure 3. The results for both types of dyes are presented in Figure 4.

For 5CB, the clearing point temperature (309 K) is very close to the measurement one (299 K) and due to that, the numerical results are not reliable, as in the case of GR-41 ($T_C = 335$ K). The Flory model tends to overestimate values of s near the clearing point.[3]

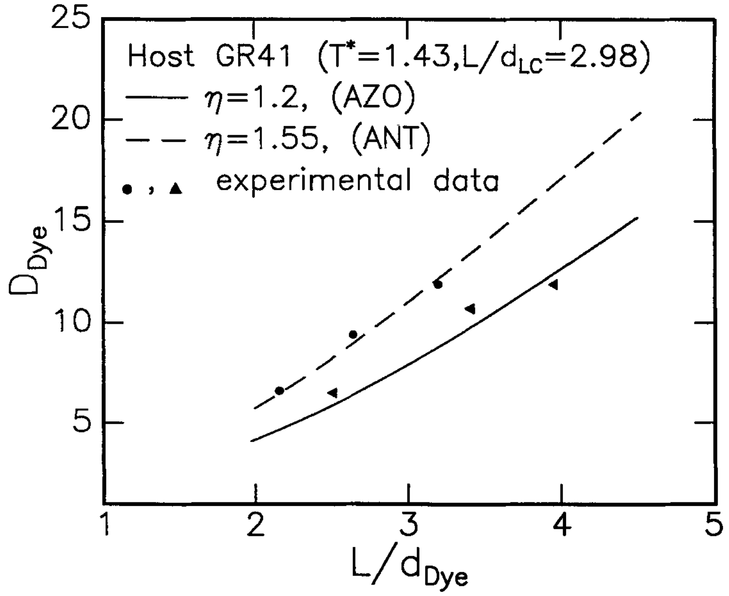

FIGURE 3 Azo- and ANT- type dyes in the GR-41 matrix. The relation between the steric (*L*/*d*) and dichroic (D_{Dye}) parameters. Lines denote the model fit.

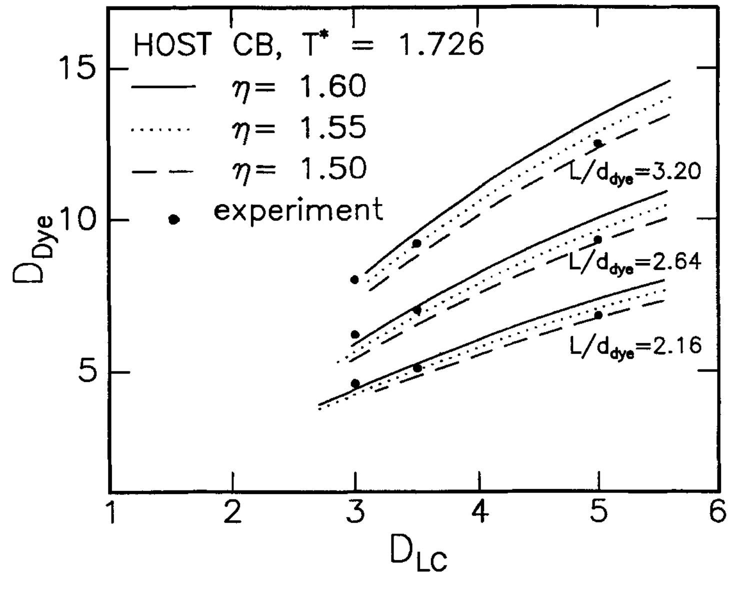

FIGURE 4 Azo- and ANT- type dyes in the 5CB matrix. The relation between the steric (*L*/*d*) and dichroic (D_{Dye}) parameters. Lines denote the model fit.

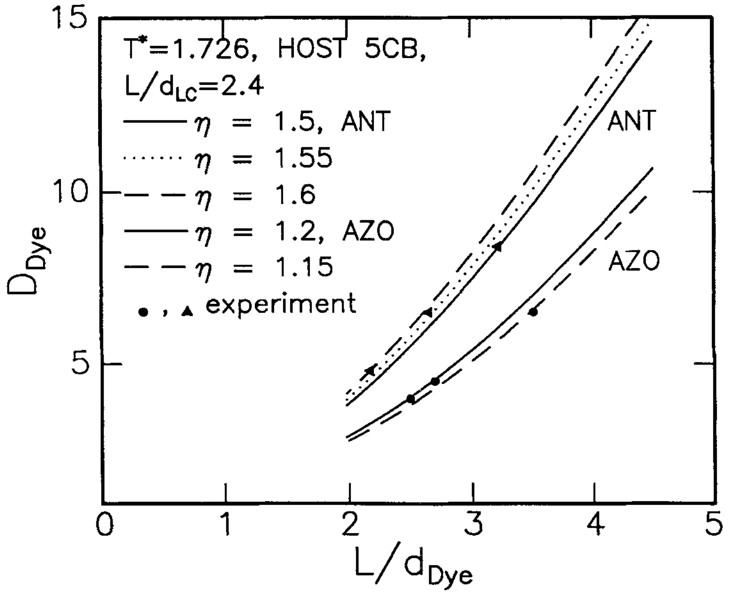

FIGURE 5 The relations between the orientational orders of dyes D_{Dye} and LC matrices, D_{LC}. Curves correspond to the numerical results.

Finally, based on above considerations, we calculate numerically the D_{Dye} as a function of D_{LC}, Figure 5. The results show good agreement between the theory and experiment, although some discrepancies for the 5CB host ($D_{\mathrm{LC}} = 3$) are observed.

Since good agreement of the calculated values and the measured ones was obtained, we studied numerically the influence of several factors on the dichroic properties of the dyes molecules. For further studies we chose the GR-41 model matrix as the more reliable one.

From the figures (Figure 6–Figure 8), as well as from the previous ones, the almost proportional dependence of D_{Dye} on the dye steric parameter is confirmed. In Figure 6 a disordering influence of the temperature increase is shown. Then we studied change induced by the different guest ratios in the mixtures, which pictured in Figure 7.

In Figure 8 we vary the density of the whole system. These changes correspond to adding some non interacting impurities (a neutral solvent) to the substance considered. As a most promising one, Figure 9, we calculate changes caused by some additional dopant. Since generally a non-interacting dopant has the disordering effect on the dyes (Figure 8) we add a very strongly interacting dopant, for example, a rod-like polymer molecule whose high anisotropy may have the ordering effect on the dyes.

The developed theory is very general and allows for study of mixtures of apriori chosen number of species.[4,5] In Figure 9 we show the change of the D_{Dye} as a function of the dopant $L_{\mathrm{LD}}/d_{\mathrm{LD}}$ ratio. The soft-, nematic interaction is assumed to be the same as for dyes and LC molecules, i.e. $\eta_{\mathrm{Dye}} = \eta_{\mathrm{LD}}$.

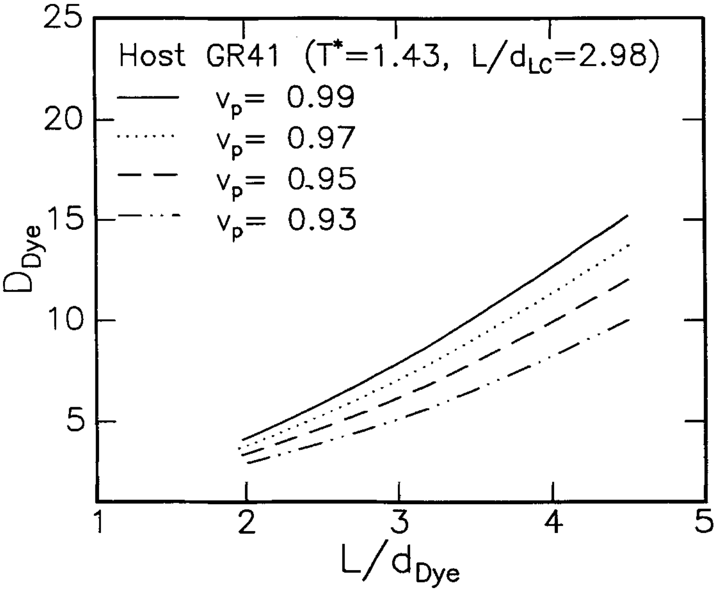

FIGURE 6 Numerical study of the temperature changes of the D_{Dye} vs. L/d_{Dye} in the AZO-GR41 system.

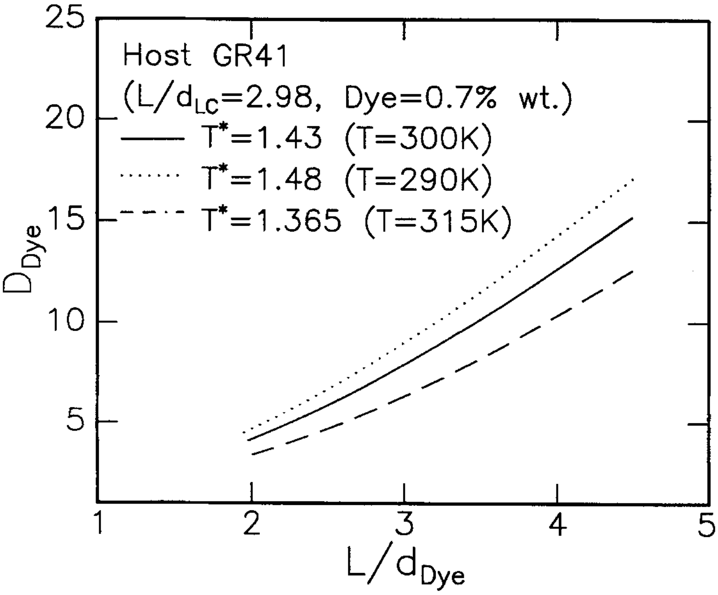

FIGURE 7 Numerical study of the influence of the dyes ratio on the D_{Dye} vs. L/d_{Dye} in the AZO-GR41 system.

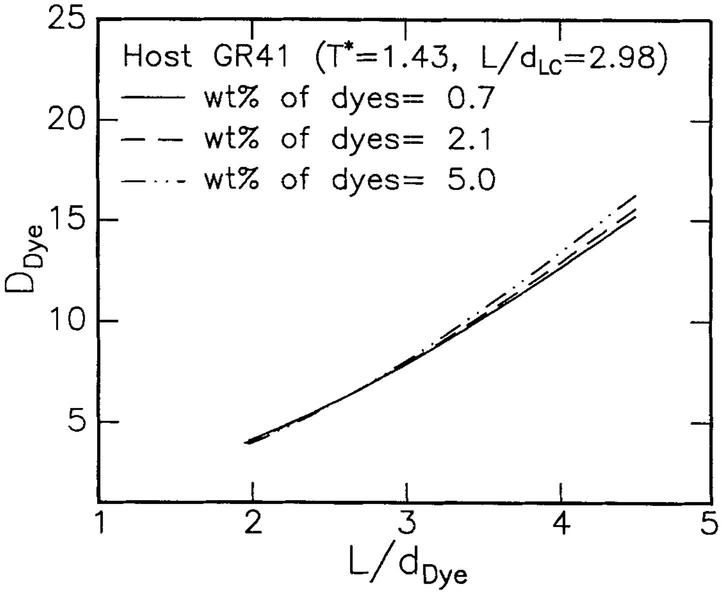

FIGURE 8 Numerical study of the density (v_p) inflicted changes of the D_{Dye} vs. L/d_{Dye} in the AZO-GR41 system.

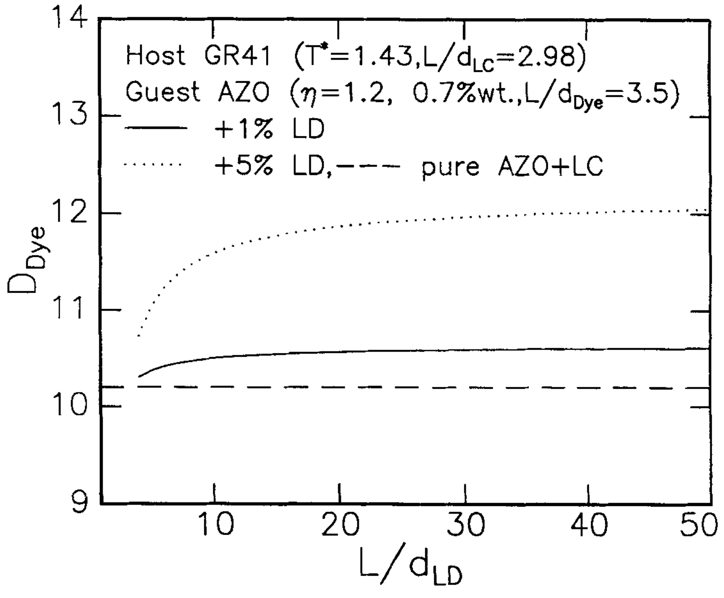

FIGURE 9 The influence of the long, stiff dopant. D_{Dye} vs. the dopant anistropy ($L_{\mathrm{LD}}/d_{\mathrm{LD}}$) for the dopant concentrations.

4. CONCLUSIONS

The calculated model curves agree very well with the experimental results, which allows us to use the model for further studies. Especially interesting is acceptable agreement of numerical results and experimental data in case of Figure 5 in comparison to the previous treatment.[2] On that basis the assumption of proportional relations between the soft, nematic interactions and the steric parameter (L/d) seems to be correct as well in case of LC as for dyes molecules.

Besides the earlier relation between the (L/d_{Dye}) and D_{Dye} we also note that the increase of the constant η, describing the "unit" nematic interaction of the molecule, results in serious growth of the D_{Dye} values (Figure 3, curves for AZO- and ANT respectively). Further we study the temperature variation of the system. The data obtained seem to be in agreement with other studies.[8] Since the decrease of temperature results in decrease of order parameter, the similar relation is observed in Figure 6.

The Figure 7 confirms that the mixture properties are almost insensitive on the guest ratio variation. Even the 10 times increase of the dyes concentration causes very small changes, especially in comparison with those caused by temperature. The changes vary according to the steric properties of the dyes. If the L/d_{Dye} is smaller than the LC then the D_{Dye} value decreases and opposite for the $L/d_{\mathrm{Dye}} > \mathrm{L}/\mathrm{d}_{\mathrm{LC}}$ (Figure 7).

The non interacting impurities in the guest-host mixture result in a very strong decrease of the D_{Dye} (Figure 8). The 5% concentration of impurities causes about 40% drop of the dye's dichroic ratio.

To improve the dichroic properties of the guest-host displays, the molecules used-should posses high anisotropy L/d and high polarizability (nematic interactions). These considerations concern the LC molecules as well as the dyes.

The increase of the dye's ratio does not improve the properties, especially in comparison with the changes inflicted by temperature variation. Since the commonly used LC and dyes have fixed steric and molecular interaction parameters there is no simple way of improvement as far as the dichroic ratio is considered. The LC built of molecules of high anisotropy and having high values of order parameter are not transparent and often freeze in room temperatures.

One possible way to solve the problem might be adding of some strongly interactive impurities, able to compensate the decrease of the D_{Dye} value. Since the ratio of the impurities may be small (2% wt.) they should not inflict the transmissive properties of the substance but might enlarge the D_{Dye} value (Figure 9). From the numerical results we notice that the influence of the dopant saturates at about $L_{\mathrm{LD}}/d_{\mathrm{LD}} = 20$, so molecules of this anisotropy might be most efficient. Although the improvement due to the steric interactions is small if the dopant molecules also interact strongly via the Maier–Saupe potential (stronger than dye-LC interaction) it will also contribute to the improvement of the dichroic ratio of the mixture. The only important problem is to find the suitable dopant with good mixing properties.

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