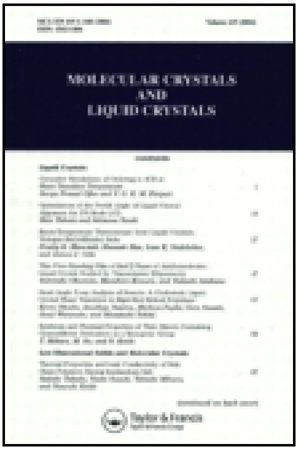

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A Theory of Temperature Dependent Switching Transition in Mixed Liquid Crystals of Opposite Diamagnetic Anisotropies

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A Landau type theory of the switching transition observed as a function of temperature in mixed liquid crystals of opposite diamagnetic anisotropies is presented. The theory is also extended to explain the nematic to isotropic transition of the mixture, which occurs at another critical temperature. The theory explains experimental results for the mixture *N*-(*p*-ethoxybenzylidene)-*p*-*n*-butylaniline (EBBA) and a ternary eutectic mixture of propyl, pentyl and heptyl bicyclohexyl carbonitrile (ZLI-1167) obtained by NMR using a probe molecule such as acetonitrile. The agreement between the theoretical and experimental results is satisfactory.

INTRODUCTION

A Landau type theory has been proposed to explain the concentration dependent switching transition in liquid crystal mixtures of opposite diamagnetic anisotropies.[1,2] The theory explains the switching transition and the behavior of the observed order parameter obtained with the help of NMR data of probe molecules (e.g., benzene or acetonitrile) dissolved in the mixture of *N*-(*p*-ethoxybenzylidene)-*p*-*n*-butylaniline

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(EBBA), which has positive diamagnetic anisotropy, and a ternary eutectic mixture of propyl, pentyl and heptyl bicyclohexyl carbonitrile (ZLI-1167) which has negative diamagnetic anisotropy.[3,4] The theory also explains the results for other mixtures such as ZLI-1167 and S-1114 (trans-*p*-pentyl-4(4-cyanophenyl)-cyclohexane).[5]

In the present paper we intend to extend the theory to temperature dependent switching as well as to the transition between the nematic and isotropic phases. As pointed out in our earlier papers,[1,2] the orientation of the probe molecules (e.g., acetonitrile) follows the orientation of the liquid crystal solvent molecules.

FORMULATION OF THE THEORY

It is well known that liquid crystals having positive diamagnetic anisotropy (e.g., EBBA) orient in the magnetic field with the optic axis aligned preferentially along the direction of the magnetic field. This is in contrast to those liquid crystals which have negative diamagnetic anisotropy (e.g., ZLI-1167) for which the overall alignment of the liquid crystal director is perpendicular to the magnetic field. In a mixture of these two types of liquid crystals, the free energy functional F must depend upon the temperature and two order parameters: $S_1 = \frac{1}{2}(3\cos^2\theta_Z - 1)$ for ZLI-1167 and $S_2 = \frac{1}{2}(3\cos^2\theta_E - 1)$ for EBBA. The symbols Z or E are used to describe ZLI-1167 and EBBA respectively, hereafter. Thus, for a fixed concentration of the components, the free energy function $F(S_1, S_2, T)$ of the system can be expanded in powers of order parameters as:

$$F = F_0 - A_1\left(1 - \frac{T}{T_c}\right)S_1^2 + B_1S_1^4 - A_2\left(1 - \frac{T}{T_c}\right)S_2^2 + B_2S_2^4 + C_1\langle S_2^2\rangle S_1^2 + C_2\langle S_1^2\rangle S_2^2 + \cdots \tag{1}$$

where A_i, B_i and C_i are the coefficients.

For the terms that are coupled, i.e., those involving $S_1^2S_2^2$, etc., we have used our previous approximation[1,2] in which the average of S_i^2 of one of the order parameters is taken, e.g., $\langle S_2^2\rangle S_1^2$, etc.; T_c is the switching temperature. Minimization of the free energy with respect to S_1 or S_2 gives the value of the order parameters S_{10} and S_{20} at the minimum of the free energy regions dominated by Z or E, respectively:

$$S_{10} = -\left[\left(\frac{A_1}{2B_1}\right)\left(1 - \frac{T}{T_c}\right) - \left(\frac{C_1}{2B_1}\right)\langle S_2^2\rangle\right]^{1/2} \tag{2}$$

$$S_{20} = \left[\left(\frac{A_2}{2B_2}\right)\left(1 - \frac{T}{T_c}\right) - \left(\frac{C_2}{2B_2}\right)\langle S_1^2\rangle\right]^{1/2} \tag{3}$$

where

$$\langle S_2^2\rangle = \left(\frac{T}{T_c}\right)h\left(1 - \frac{T}{T_c}\right) \tag{4}$$

$$\langle S_1^2\rangle = \left(\frac{T_c}{T}\right)h\left(1 - \frac{T_c}{T}\right) \tag{5}$$

where $h(x)$ is the step function

$$h(x) = 0 \quad \text{for } x < 0$$
$$h(x) = 1 \quad \text{for } x > 0$$

This is similar to our earlier formulation for the case of concentration dependent switching.

Expanding F about S_{10} gives

$$F = F(S_{10}) + \tfrac{1}{2}F''(S_{10})\left(\tfrac{3}{2}\cos^2\theta - \tfrac{1}{2} - S_{10}\right)^2 + \cdots \tag{6}$$

where $F'' = \partial^2 F/\partial S_1^2$.

The overall effective order parameter, $\langle \tfrac{3}{2}\cos^2\theta - \tfrac{1}{2}\rangle$, in each region is calculated from the relation

$$\langle\cos^2\theta\rangle = \int_0^1 \cos^2\theta \exp\left(-\frac{F}{k_BT}\right)d(\cos\theta)\Big/\int_0^1 \exp\left(-\frac{F}{k_BT}\right)d(\cos\theta) \tag{7}$$

Expansion of the exponential and then evaluation of the integrals give the order parameter of the mixture for the Z-dominated region as

$$S_Z = \langle \tfrac{3}{2}\cos^2\theta - \tfrac{1}{2}\rangle_Z$$
$$= \frac{\dfrac{1}{2} - \left(\dfrac{6}{T}\right)\left(\dfrac{B_1}{k_B}\right)S_{10}^2\left[\dfrac{9}{28} + \dfrac{(S_{10} + \frac{1}{2})^2}{3} - \dfrac{3}{5}\left(S_{10} + \dfrac{1}{2}\right)\right]}{1 - \left(\dfrac{4}{T}\right)\left(\dfrac{B_1}{k_B}\right)S_{10}^2\left[\dfrac{9}{20} + \left(S_{10} + \dfrac{1}{2}\right)^2 - \left(S_{10} + \dfrac{1}{2}\right)\right]} - \frac{1}{2} \tag{8}$$

At $T = T_c$, S_{10} and also S_Z Eq. (8) become zero, in agreement with the coexistence of both orientations. Expansion of F about S_{20} and the evaluation of $\langle \cos^2\theta \rangle$ again give the order parameter S_E of the mixture for the E-dominated region as

$$S_E = \langle \tfrac{3}{2}\cos^2\theta - \tfrac{1}{2} \rangle_E$$

$$= \frac{\dfrac{1}{2} - \left(\dfrac{6}{T}\right)\left(\dfrac{B_2}{k_B}\right) S_{20}^2 \left[\dfrac{9}{28} + \dfrac{(S_{20} + \frac{1}{2})^2}{3} - \dfrac{3}{5}(S_{20} + \tfrac{1}{2})\right]}{1 - \left(\dfrac{4}{T}\right)\left(\dfrac{B_2}{k_B}\right) S_{20}^2 \left[\dfrac{9}{20} + \left(S_{20} + \dfrac{1}{2}\right)^2 - \left(S_{20} + \dfrac{1}{2}\right)\right]} - \frac{1}{2} \tag{9}$$

At $T = T_c$, S_{20} and also S_E, Eq. (9) become zero, again in agreement with the experimental observation.

The nematic mixture turns into isotropic at a temperature T_k above T_c. It is well known that the Landau theory is applicable near the transition temperature. Accordingly we have to develop another expression for the second transition, i.e., nematic to isotropic. The free energy of the mixture for the region near T_k can be expressed as

$$F' = F_0' - A_1'\left(1 - \frac{T}{T_k}\right) S_1^2 + D_1' S_1^3 + B_1' S_1^4 - A_2'\left(1 - \frac{T}{T_k}\right) S_2^2$$
$$+ D_2' S_2^3 + B_2' S_2^4 + C_1' \langle S_2^2 \rangle S_1^2 + C_2' S_2^2 \langle S_1^2 \rangle + \cdots \tag{10}$$

where we have introduced third order terms in S_1 and S_2 inasmuch as this phase transition is weakly of first order.[6] Minimization of F' with respect to S_2 leads to the value of S_2 at the minimum free energy as

$$S_{2m} = -\frac{3}{8}\left(\frac{D_2'}{B_2'}\right) + \left[\frac{9}{64}\left(\frac{D_2'}{B_2'}\right)^2 + \left(\frac{A_2'}{2B_2'}\right)\left(1 - \frac{T}{T_k}\right) - \left(\frac{C_2'}{2B_2'}\right)\langle S_1^2 \rangle\right]^{1/2} \tag{11}$$

Substitution of $(T/T_k)h(1 - T/T_k)$ for $\langle S_1^2 \rangle$, expansion of F' about S_{2m}, and the evaluation of $\langle \cos^2\theta \rangle$ lead to an expression for the order parameter S_{NI} of the mixture in the region near T_k:

$$S_{NI} = \langle \tfrac{3}{2}\cos^2\theta - \tfrac{1}{2} \rangle_{NI}$$

$$= \frac{\frac{1}{2} - (1 \cdot 5/T)\left[4\left(\frac{B_2'}{k_B}\right)S_{2m}^2 + 1.5\left(\frac{D_2'}{k_B}\right)S_{2m}\right]\left[\frac{9}{28} + \frac{\left(S_{2m} + \frac{1}{2}\right)^2}{3} - \frac{3}{5}\left(S_{2m} + \frac{1}{2}\right)\right]}{1 - \left(\frac{1}{T}\right)\left[4\left(\frac{B_2'}{k_B}\right)S_{2m}^2 + 1.5\left(\frac{D_2'}{k_B}\right)S_{2m}\right]\left[\frac{9}{20} + \left(S_{2m} + \frac{1}{2}\right)^2 - \left(S_{2m} + \frac{1}{2}\right)\right]} - \frac{1}{2} \tag{12}$$

At $T = T_k$, S_{2m} and also S_{NI}, Eq. (12) become zero, which is consistent with the experimental results.

COMPARISON WITH EXPERIMENTAL RESULTS

The order parameter values for the nematic mixture have been extracted from the observed dipolar couplings (D_{ij}) from proton NMR spectra at different temperatures. The expressions

$$S_{ij} = D_{ij} \Big/ \left[-\frac{k}{\langle r_{ij}^3 \rangle} \right]$$

where $k = 120067$ Hz Å^3 for a pair of protons, $\langle r_{ij}^3 \rangle = (1.80\ \text{Å})^3$ for methyl protons in acetonitrile, $S_{c_3} = -2\ S_{HH}$ have been used in extracting the order parameter. The data points thus obtained are further normalized by dividing them by the largest data point in each region (separately in the regions dominated by Z and E). The coefficients to be determined are A_1, B_1, C_1, A_2, B_2, C_2, A_2', B_2', C_2', and D_2'. It is not possible to calculate them from first principles. They have been estimated to agree with the normalized data.

Their values are:

$$\left(\frac{B_1}{k_B}\right) = 259.25, \qquad \left(\frac{A_1}{2B_1}\right) = 0.2684,$$

$$\left(\frac{C_1}{2B_1}\right) = -0.2473, \qquad \left(\frac{B_2}{k_B}\right) = 46.6343,$$

$$\left(\frac{A_2}{2B_2}\right) = -0.9353, \qquad \left(\frac{C_2}{2B_2}\right) = -1.0007,$$

$$\left(\frac{B_2'}{k_B}\right) = 46.6343, \qquad \left(\frac{D_2'}{k_B}\right) = 0.04663,$$

$$\left(\frac{A_2'}{2B_2'}\right) = 2.720, \qquad \left(\frac{C_2'}{2B_2'}\right) = -0.940.$$

These have the expected signs, i.e., $A_1 > 0$, $B_1 > 0$, $C_1 < 0$, $A_2 < 0$, $B_2 > 0$, $C_2 < 0$, $A_2' > 0$, $B_2' < 0$, $C_2' < 0$, $D_2' > 0$ so that the overall sign of the coefficients $[-A_1(1 - T/T_c)]$, $[-A_2(1 - (T/T_c))]$ and $[-A_2'(1 - (T/T_k))]$ in Eqs. (1) and (10) are negative as required by the Landau criterion[7] of a minimum at a non-zero value of the order parameter.

The theoretically calculated and experimentally observed values of the order parameter for various temperatures are shown on the same graph for comparison (Figure 1). The agreement between theory and experiment is satisfactory. It has the right trend and shows switching of the order parameter at the critical temperature T_c. It also shows the

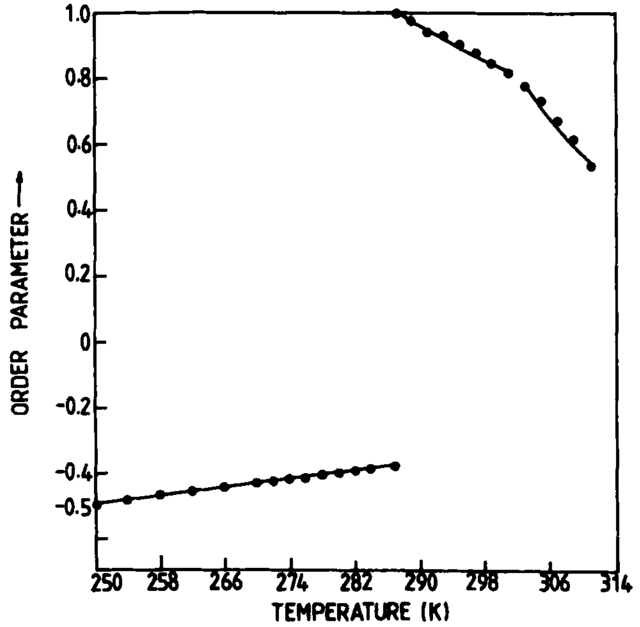

FIGURE 1 Calculated and experimental plots of the order parameter as function of temperature of mixed liquid crystals. Acetonitrile in ZLI-1167 + EBBA. (● experimental point, — theoretical curve).

transition from the nematic to the isotropic phase at the transition temperature T_k.

The theoretically calculated order parameter values for the temperature range $T_c \leq T < (T_c + 14\ \mathrm{K})$ from Eq. (9) agree with experimentally observed values. Beyond $(T_c + 14\ \mathrm{K})$ the calculated values start deviating from the observed values. This is due to the mixture system heading towards another transition (nematic to isotropic observed at $T_k = 313$ K). So the Eq. (12) has been used for the range $(T_c + 14\ \mathrm{K}) \leq T \leq T_k$ to obtain the calculated values. In this region, too, the agreement with experimental data is good.

CONCLUDING REMARKS

In the foregoing section, we have presented a Landau type theory for the behavior of the order parameters in mixed nematic liquid crystals of opposite anisotropies as a function of temperature at fixed concentration. At a critical temperature T_c the orientation of the liquid crystal director relative to the applied magnetic field switches from perpendicular to parallel. At T_c both orientations coexist. Further on, at a temperature T_k, the system shows a transition from the nematic to the isotropic phase which is weakly of the first order. Assuming applicability of the Landau theory, we have proposed theoretical expressions valid in the two transition regions. The agreement between theory and the experimental results obtained from NMR studies is satisfactory. The theoretical calculations show that the overall effective order parameter $S_{eff} = \langle \frac{3}{2}\cos^2\theta - \frac{1}{2} \rangle$ in each region considered depends on the competition between two order parameters of the constituents S_1 and S_2. The fact that they coexist suggests that there are local inhomogeneities (i.e., clusters) of each component. The theoretical expressions for the overall effective order parameters do indeed depend on the values of the order parameter of the individual species (cf. Eqs. (8), (9) and (2) and (3), (11) and (12). This is a clear example of a mixed system where the order parameters of the components are coupled.

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