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

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

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A macroscopic theory of switching transition in a liquid crystal mixture of two thermotropic nematic systems of opposite diamagnetic anisotropies is presented. This is based on Landau theory and shows that temperature being fixed, a transition occurs at a critical relative concentration of the two liquid crystals under consideration. The theoretical dependence of the relevant order parameters is in good agreement with recently observed experimental results on such mixtures.

1. INTRODUCTION

That structural phase transition in crystalline solids takes place at a critical concentration of some distorting ions has been known for some time.[1] Recently it has been shown by Khetrapal and Kunwar[2,3] that mixtures of two thermotropic nematic liquid crystals with opposite diamagnetic anisotropies display a switching transition from one orientation to another at a critical ratio of the relative concentrations of the two liquid crystals in the mixture. At the critical concentration the optic axis of the liquid crystal mixture rotates by 90° with respect to the applied magnetic field. The experiment involves the study of proton NMR of probe molecules (*e.g.*, benzene) dissolved in the solvent mixture of ZL1-1167 (a ternary eutectic mixture of propyl, pentyl and heptyl bicyclohexyl carbonitrile) which has negative diamagnetic anisotropy and EBBA, *N*-(*p*-ethoxy benzylidene)-*p*-*n*-butylaniline, having positive diamagnetic anisotropy. In one hundred percent ZL1-1167 system, the results show that the optic axis has an overall perpendicular orientation with respect to the applied magnetic field. On the other hand, in pure EBBA the orientation of the optic axis is parallel to the applied magnetic field. A plot of the dipolar coupling between the protons i and j (D_{ij}) of the solute molecule (*e.g.*, benzene) as a function of relative concentrations of EBBA and ZL1-1167 (hereafter referred to as E and Z respectively) shows a sudden change in the sign and the magnitude of D_{ij} at about the critical ratio 25:75. This change is half or twice depending on the direction of approach of the critical point. This is akin to a phase transition in the sense of Haken.[4] In another set of experiments where the ratio of the mixture is not changed but the temperature is varied, one sees a similar change in the sign and the magnitude of D_{ij} at a critical temperature.[3] In fact at some values of temperature and concentration the spectra of the two phases coexist.

The dipolar coupling in the liquid crystal mixture can be expressed as[5]

$$D_{ij} = -\frac{K}{\langle r_{ij}^3 \rangle} S_{ij}(x_E, x_Z, T) \tag{1}$$

where $K = (h\gamma_i\gamma_j/4\pi^2)$ is a constant for a pair of nuclei, γ_i being the gyromagnetic ratio of the i^{th} nucleus and r_{ij} is the distance between the nuclei i and j. $S(x_E, x_Z, T)$ is the effective order parameter in the liquid crystal mixture, x_E and x_Z being the concentration ratio with the critical value of E and Z. Explicitly it has the form

$$S(x_E, x_Z, T) = S_{ij}\frac{1}{2}\langle 3\cos^2\theta - 1\rangle \tag{2}$$

where

$$S_{ij} = \frac{1}{2}\langle 3\cos^2\theta_{ij} - 1\rangle \tag{3}$$

θ_{ij} being the angle between the position vector r_{ij} and the optic axis of the mixture. We assume that this always follows the orientation of the liquid crystal molecule. Thus the crucial effective order parameter becomes $\frac{1}{2}\langle 3\cos^2\theta - 1\rangle$, θ being the angle of the optic axis of the mixture with respect to the external magnetic field. Accordingly, we are required to calculate $S(x_E, x_Z, T)$, i.e.,

$$\frac{1}{2}\langle 3\cos^2\theta - 1\rangle . \tag{4}$$

In point of fact this amounts to calculating $\langle\cos^2\theta(x_E, x_Z, T)\rangle$. As remarked earlier, in pure (E) and pure (Z), the orientation of the liquid crystal optic axes are parallel and perpendicular respectively with respect to the external magnetic field. The mixture of the two liquid crystals will be subject to two competing order parameters. We call these $S_1 = (\frac{3}{2}\cos^2\theta_Z - \frac{1}{2})$ for ZLI-1167 and $S_2 = (\frac{3}{2}\cos^2\theta_E - \frac{1}{2})$ for EBBA.

2. THEORETICAL FORMULATION

In analogy with superconductors, a Landau type theory of phase transition in liquid crystals has been considered by several authors.[6–9] In the present paper, we develop a simple Landau theory of liquid crystal mixtures consisting of two order parameters (S_1, S_2). The free energy function $F(S_1, S_2, T)$ of the system can be expanded in powers of order parameters as

$$F = F_0 + F_1S_1^2 + F_2S_1^4 + F_3S_2^2 + F_4S_2^4 + 2F_5S_1^2S_2^2 + \ldots . \tag{5}$$

In the present treatment we shall work at a fixed temperature (T). Thus, we introduce the function

$$\begin{aligned} F = F_0 &+ A_1(x_E, x_Z)S_1^2 + B_1(x_E, x_Z)S_1^4 \\ &+ A_2(x_E, x_Z)S_2^2 + B_2(x_E, x_Z)S_2^4 \\ &+ 2C_{12}(x_E, x_Z)S_1^2S_2^2 + \ldots . \end{aligned} \tag{6}$$

In the above the coefficients of the various powers of order parameter are functions of concentration ratios of the components defined as

$$x_E = \alpha_E/\alpha_{CE} \text{ for (E)} \quad \text{and} \quad x_Z = \alpha_Z/\alpha_{CZ} \text{ for (Z)},$$

α_E denoting concentration, α_{CE} being its value at the critical point. For order to develop, the coefficients such as A_1 should be negative below the critical concentration. Accordingly, Eq. (6) can be recast as

$$\begin{aligned} F = F_0 &- a(1 - x_E)S_1^2 + bS_1^4 - A(1 - x_Z)S_2^2 \\ &+ BS_2^4 + C_1\langle S_2^2\rangle S_1^2 + C_2\langle S_1^2\rangle S_2^2 \end{aligned} \tag{7}$$

The term involving the coupling between the two order parameters $(2C_{12}S_1^2S_2^2)$ has been further simplified by taking the average value of one of the order parameters. Minimization of the function F with respect to S_2 gives the condition for the ordered phase:

$$S_{20} = \left[\frac{A(1 - x_Z) - C_2\langle S_1^2\rangle}{2B}\right]^{1/2} \tag{8}$$

in the EBBA dominating region. Further, we shall require the second derivative of the function F with respect to S_2 at the minimum. We get

$$\left[\frac{\partial^2 F}{\partial S_2^2}\right]_{S_2=S_{20}} = 4[A(1 - x_Z) - C_2\langle S_1^2\rangle] \tag{9}$$

The condition that S_{20} represents a minimum is that $A > 0$ and $A(1 - x_Z) > C_2\langle S_1^2\rangle$ or $C_2 < 0$. For computing the average value of $\cos^2\theta$ we make use of the expression

$$\langle\cos^2\theta\rangle = \int_0^1 \cos^2\theta \exp\left(-\frac{F}{K_BT}\right) d(\cos\theta) \Big/ \int_0^1 \exp\left(-\frac{F}{K_BT}\right) d(\cos\theta) \tag{10}$$

where the limits vary from 0 to 1 inasmuch as the directions n and $-n$ of the liquid crystal optic axis (i.e., the director) are equivalent.[7] Also in the experiment the observed change in the orientation of the optic axis is from 0 to 90° with respect to the magnetic field. For evaluating the integrals involved in Eq. (10), we resort to expansion in powers of $(\tfrac{3}{2}\cos^2\theta - \tfrac{1}{2} - S_{20})$ up to second order. This gives

$$\langle\cos^2\theta\rangle = \frac{\int_0^1 \cos^2\theta \exp\left[-F''(S_{20})\left(\frac{3}{2}\cos^2\theta - \frac{1}{2} - S_{20}\right)^2 / 2K_BT\right] d(\cos\theta)}{\int_0^1 \exp\left[-F''(S_{20})\left(\frac{3}{2}\cos^2\theta - \frac{1}{2} - S_{20}\right)^2 / 2K_BT\right] d(\cos\theta)}$$

Again expanding the exponential and integrating, we get

$$\langle\cos^2\theta\rangle = \frac{\frac{1}{3} - 4(B/K_BT)S_{20}^2\left[\frac{9}{28} + \frac{(S_{20} + \frac{1}{2})^2}{3} - \frac{3}{5}\left(S_{20} + \frac{1}{2}\right)\right]}{1 - 4(B/K_BT)S_{20}^2\left[\frac{9}{20} + \left(S_{20} + \frac{1}{2}\right)^2 - \left(S_{20} + \frac{1}{2}\right)\right]} \tag{12}$$

In EBBA dominated region (before the transition) we choose the value of $C_2\langle S_1^2\rangle$ as

$$C_2\langle S_1^2\rangle = C_2 x_Z h(1 - x_Z), \tag{13}$$

where $h(y)$ is a step function and is zero for a negative value of the argument and unity for positive values. The expression for the corresponding effective order parameter turns out to be

$$\frac{3}{2}\langle\cos^2\theta\rangle - \frac{1}{2} =$$

$$\frac{\frac{1}{2} - 6(B/K_BT)S_{20}^2\left[\frac{9}{28} + \frac{(S_{20}+\frac{1}{2})^2}{3} - \frac{3}{5}\left(S_{20}+\frac{1}{2}\right)\right]}{1 - 4(B/K_BT)S_{20}^2\left[\frac{9}{20} + \left(S_{20}+\frac{1}{2}\right)^2 - \left(S_{20}+\frac{1}{2}\right)\right]} - \frac{1}{2} \qquad (14)$$

It should be noted that at the point of transition, i.e., $x_Z = 1$, the above expression i.e., Eq. (14) gives zero as expected. This implies the coexistence of both types of orientations as observed experimentally.

In the Z-dominated region, minimization of F with respect to S_1 gives

$$S_{10} = -\left[\frac{a(1-x_E) - C_1\langle S_2^2\rangle}{2b}\right]^{1/2} \qquad (15)$$

A derivation similar to the case that led to Eq. (12) then gives:

$$\langle\cos^2\theta\rangle = \frac{\frac{1}{3} - 4(b/K_BT)S_{10}^2\left[\frac{9}{28} + \frac{(S_{10}+\frac{1}{2})^2}{3} - \frac{3}{5}\left(S_{10}+\frac{1}{2}\right)\right]}{1 - 4(b/K_BT)S_{10}^2\left[\frac{9}{20} + \left(S_{10}+\frac{1}{2}\right)^2 - \left(S_{10}+\frac{1}{2}\right)\right]} \qquad (16)$$

In the Z-dominated region also we use $C_1\langle S_2^2\rangle = C_1 x_E h(1 - x_E)$. Thus the corresponding order parameter becomes

$$\frac{3}{2}\langle\cos^2\theta\rangle - \frac{1}{2} =$$

$$\frac{\frac{1}{2} - 6(b/K_BT)S_{10}^2\left[\frac{9}{28} + \frac{(S_{10}+\frac{1}{2})^2}{3} - \frac{3}{5}\left(S_{10}+\frac{1}{2}\right)\right]}{1 - 4(b/K_BT)S_{10}^2\left[\frac{9}{20} + \left(S_{10}+\frac{1}{2}\right)^2 - \left(S_{10}+\frac{1}{2}\right)\right]} - \frac{1}{2} \qquad (17)$$

which at $x_E = 1$ gives zero at the critical point.

A few words about the Landau theory will be in order. Although the expansion of the free energy (function F here) in terms of the order parameters is supposed to be carried out near the critical point, the recent experience on the coexistence of magnetic and superconducting orders shows that the range of validity (in this case the Ginzburg-Landau theory) is much larger.[10,11] Accordingly, in our present formulation, we have used the Landau theory in this wider context. However, parameters such as $(1 - x_E)$, $(1 - x_Z)$, x_E, x_Z, never exceed unity.

3. COMPARISON WITH EXPERIMENTAL RESULTS

In order to compare the above theory with experimental data, we first extract the values of the observed ordered parameter by dividing the measured data by the appropriate constant, i.e.,

$$D_{ij}\left(-\frac{K}{\langle r_{ij}^3\rangle}\right)^{-1},$$

where $K = 120067$ (hertz × Å^3) for a pair of protons and $\langle r_{ij}^3\rangle = (2.481\ \text{Å})$.[3] The data points thus obtained are further normalized by dividing by 0.1236 in the Z-dominated region (up to the critical point) and by 0.10012 in the E-dominated region from the initial point to 100% EBBA. These normalization constants correspond to the experimental values.

The coefficients to be determined in the EBBA dominated region are $(A/2B)$, (B/K_BT), $(C_2/2B)$ and in the Z-dominated region are $(a/2b)$, (b/K_BT), $(C_1/2b)$. It is not possible to calculate them from first principles. Accordingly, they are estimated so as to have agreement with normalized data. The values for the E-dominated region are: $(A/2B) = 0.8987$ $(B/K_BT) = 0.162$, and $(C_2/2B) = -1.0065$. These have the expected sign i.e., $B > 0$, $A > 0$, and $C_2 < 0$ so that the overall sign of the coefficient of S_2^2 is negative as demanded by the Landau criterion[6] of a minimum at a non-zero value of S_2.

On the other hand, for the Z-dominated region we have $(a/2b) = 0.25$, $(b/K_BT) = 1.037$ and $(C_1/2b) = -0.2385$. This is also consistent with Landau[6] criterion as the minimum here occurs at S_{10} and the coefficient of S_1^2 in Eq. (7) should be negative.

A plot of the theoretical graph obtained using the above parameters is given in Figure 1 along with experimental data points for benzene.[2] The agreement is extremely satisfactory. It has the right trend and shows switching of the order parameters near the critical concentration. At the critical concentration, the overall order parameter is zero implying the coexistence of the two types of orientation in agreement with the experiment.

4. CONCLUDING REMARKS

In the foregoing sections, we have presented a theory of concentration-dependent switching transition in a liquid crystal mixture of opposite

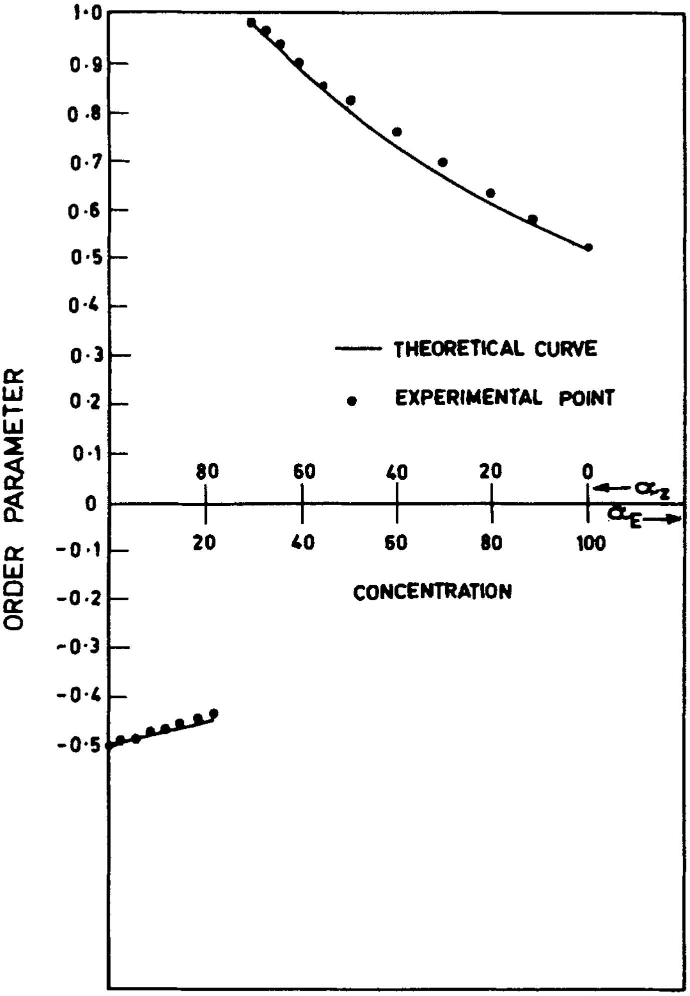

FIGURE 1 A plot of the order parameter vs relative concentrations of the two liquid crystals.

diamagnetic anisotropies with two order parameters. It is based on the Landau theory wherein the free energy function (in fact F as the temperature is fixed) is expanded in powers of the relevant order parameters, *e.g.*, S_1 and S_2 which involve the angle of orientations of the optic axis of liquid crystals in question with respect to the applied magnetic field. The quantities which are observed are related to these, namely, the effective order parameter $\frac{3}{2}\langle\cos^2\theta\rangle - \frac{1}{2}$. Theoretical expressions derived show a transition at a critical concentration $\alpha_{CE}:\alpha_{CZ}$ as reflected by the concentration parameters $x_E = (\alpha_E/\alpha_{CE})$ and $x_Z = (\alpha_Z/\alpha_{CZ})$. At the critical point both order parameters become zero. In the E-dominated region it has positive values and in the Z-dominated region it has negative values as indeed observed. The theoretical graph of order parameter (see Figure 1) is in very good agreement with experimental data points for the parameters chosen. This suggests that a Landau-like theory for the concentration dependent switching transition observed is in the right direction. A subsequent observation by Diehl and Jokisaari[12] can also be explained by the present theory. It may be noted that the experimental value of the order parameter in the E-dominating region decreases with increasing concentration. It has the maximum values near the transition point which has been normalized to unity. All these trends are in agreement with the theory presented herein.

The temperature dependence of the order parameters will be discussed in another paper along with experimental data.

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