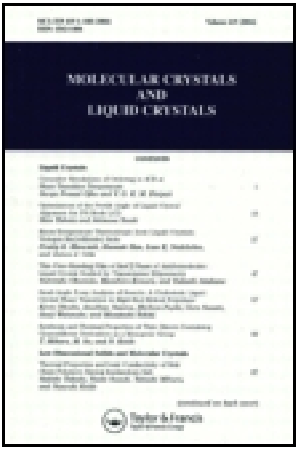

Molecular Crystals and Liquid Crystals

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MOLECULAR THEORY ON LIQUID CRYSTALLINE MIXTURES

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MOLECULAR THEORY ON LIQUID CRYSTALLINE MIXTURES

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The nematic-isotropic phase transitions in mixtures of rod-like and disc-like molecules are studied by a mean field theory. We consider both attraction and hard-core repulsion for the model molecules, thermotropic phase transitions are found from the isotropic to one of the two types of uniaxially symmetric nematic phases: optically positive N^+ and negative N^-. On the other hand, biaxially symmetric nematic phase is shown to be always less stable than the uniaxial phase. We predict that re-entrant phase transition occur for the lyotropic system.

Keywords: liquid crystal; molecular theory; phase transition; rod-disc mixture

INTRODUCTION

Various mixtures of liquid crystals have been actively used in applications. However, mixtures of molecules having extremely different shapes are not yet so well understood theoretically and experimentally.

Recent theoretical study and computer simulations found the lyotropic phase transitions between the isotropic phase and all of the two types of uniaxially symmetric nematic phases, say N^+ and N^-, and biaxially symmetric nematic phase, say Nb phases by assuming only hard-core repulsion among the molecules [1]. Palffy-Muhoray and Hoaston examined Nb phase for the system of biaxial molecules [2]. However the Nb phase, for the

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mixtures of uniaxial molecules have not yet been found experimentally for real systems [3,4].

In this paper, we study theoretically the nematic-isotropic phase transition in mixtures of rod-like and disc-like molecules. Assuming that both the attractive dispersion force and hard-core repulsion are effective among the molecules, we treat the system in the mean-field approximation. Then, we find that one of N^+ and N^- are stable depending on the mixing ratio, and Nb is always unstable compared with the uniaxial phases.

MODEL AND THEORY

Let us consider a mixture of N_R cylindrical rods with the length L_R and diameter D_R ($L_R > D_R$) and N_D circular discs with the width L_D and diameter D_D ($L_D < D_D$). We consider that the interaction potential between i and j-th molecules is the sum of the hard core repulsion and the attractive potential.

The hard-core repulsive potential is assumed as [5]

$$\phi^a_{ij} = \begin{cases} \infty : \text{if i and jth molecules intersect} \\ 0 \ \ : \text{otherwise} \end{cases} \tag{1}$$

and we assume that the attractive dispersion potential in the form [6]

$$\begin{aligned} \sum \phi^a_{ij} = &-\sum C^{RR}(r_{ij}) - \sum C^{RD}(r_{ij}) - \sum C^{DD}(r_{ij}) \\ &- \sum A^{RR}(r_{ij}) P_2(\hat{a}_{Ri}\cdot\hat{a}_{Rj}) - \sum A^{RD}(r_{ij}) P_2(\hat{a}_{Ri}\cdot\hat{a}_{Dj}) \\ &- \sum A^{DD}(r_{ij}) P_2(\hat{a}_{Di}\cdot\hat{a}_{Dj}) \end{aligned} \tag{2}$$

where r_{ij} is a the distance between the centers of molecules, $\mathbf{a}_{Ri}$ is the unit vector indicating the direction of long axis of i-th rod and $\mathbf{a}_{Di}$ indicates the direction of the plane normal of i-th disc, the suffixes RR, RD and DD mean interaction between rod-like molecules, rod and disc-like molecules and disc-like molecules, respectively. $P_2(x) = (3x^2 - 1)/2$ is the 2nd Legendre polynomial. It is to be noted that the coupling constants $C(r_{ij})$ for the isotropic interaction are all positive and for the

$$\begin{aligned} A^{RR} &\propto (\Delta\alpha_R)^2 > 0 \\ A^{RD} &\propto (\Delta\alpha_R)(\Delta\alpha_D) < 0 \\ A^{DD} &\propto (\Delta\alpha_D)^2 > 0 \end{aligned} \tag{3}$$

anisotropic terms $A(r_{ij})$ are

Denoting the component of the polarizability parallel to the molecular axis by $\alpha_{||}$, and perpendicular one by $\alpha_{\perp}$. We define the anisotropy here as $\varDelta\alpha = \alpha_{||} - \alpha_{\perp}$.

$$S_R = \left\langle \frac{1}{N_R}\sum_{i}^{N_R} P_2(\hat{n}_R \cdot \hat{a}_{Ri}) \right\rangle, \quad S_D = \left\langle \frac{1}{N_D}\sum_{i}^{N_D} P_2(\hat{n}_D \cdot \hat{a}_{Di}) \right\rangle, \tag{4}$$

The orientational order parameters S_R and S_D are defined as where $\mathbf{n}_R$ and $\mathbf{n}_D$ are directors for each molecule in the nematic phase and $\langle \ldots \rangle$ express the thermal average.

We calculate the free energy of the system as the function of order parameters using the method of symmetry breaking potential [7,8]. The result is given by

$$F_{total}(S_R, S_D) = F_{nem} + F_{mix} + F_{Iso} \tag{5}$$

$$\begin{aligned}\frac{F_{nem}}{NkT} = {} & \frac{1}{2}x^2\Gamma^{RR}S_R^2 + P_2(\hat{n}_R \cdot \hat{n}_D)x(1-x)\Gamma^{RD}S_R S_D \\ & + \frac{1}{2}(1-x)^2\Gamma^{DD}S_D^2 - x\ln I_0\left(\eta_R^0\right) - (1-x)\ln I_0\left(\eta_D^0\right)\end{aligned} \tag{6}$$

$$\begin{aligned}\frac{F_{mix} + F_{Iso}}{NkT} = {} & \frac{x^2}{2}c_R\left(8 + 2\frac{L_R}{D_R}\right) + x(1-x)\sqrt{c_R c_D}\left(8 + \frac{1}{2}\frac{D_D}{D_R}\sqrt{\frac{L_R}{L_D}}\right) \\ & + \frac{(1-x)^2}{2}c_D\left(8 + \frac{\pi}{2}\frac{D_D}{L_D}\right) \\ & + x\ln x + (1-x)\ln(1-x) + \ln\frac{N}{V} - 1 \\ & - \beta\left(\frac{x}{2}\tilde{C}^{RR} + x(1-x)\tilde{C}^{RD} + \frac{(1-x)^2}{2}\tilde{C}^{DD}\right)\end{aligned} \tag{7}$$

where F_{nem}, F_{mix} and F_{iso} are free energy terms of nematic, mixing and isotropic respectively. $n = N/V$, k the Boltzmann constant, T the absolute temperature, c_R and c_D the volume fractions for each molecules, and $x = N_R/N$ is the composition of the rods in the mixture.

Γ's indicate the part of molecular interactions contributing the orientational order. They are expressed as

$$\begin{aligned}\Gamma^{RR} &= \frac{\tilde{A}^{RR}}{kT} + \frac{5L_R}{4D_R}c_R > 0 \qquad : rod - rod, \\ \Gamma^{RD} &= \frac{\tilde{A}^{RD}}{kT} - \frac{5D_D}{8D_R}\sqrt{\frac{L_R}{L_D}}\sqrt{c_R c_D} < 0 : rod - disc, \left(\tilde{A} = n\int A(r_{ij})dr\right) \\ \Gamma^{DD} &= \frac{\tilde{A}^{DD}}{kT} + \frac{5\pi D_D}{16L_D}c_D > 0 \qquad : disc - disc,\end{aligned} \tag{8}$$

the first term of Γ's expresses the effect of attractive potential and the second the excluded volume effect due to the hard-core repulsion. We note $\Gamma^{RD} < 0$ whereas $\Gamma^{RR} > 0$ and $\Gamma^{DD} > 0$,

The order parameters of each molecule are determined by solving the simultaneous self-consistent equations that describe the condition to minimize the free energy:

$$\begin{cases} \eta_R^0 = x\Gamma^{RR} S_R + P_2(\hat{n}_R \cdot \hat{n}_D)(1-x)\Gamma^{RD} S_D \\ \eta_D^0 = P_2(\hat{n}_R \cdot \hat{n}_D)x\Gamma^{RD} S_R + (1-x)\Gamma^{DD} S_D \end{cases} \tag{9}$$

where we defined the functions

$$\begin{aligned} S_R &= \frac{I_1(\eta_R^0)}{I_0(\eta_R^0)}, \quad I_0(\eta) = \int \exp\{\eta P_2(\hat{n}_i \cdot \hat{a}_i)\} d\hat{a}_i, \\ S_D &= \frac{I_1(\eta_D^0)}{I_0(\eta_D^0)}, \quad I_1(\eta) = \frac{dI_0(\eta)}{d\eta}, \end{aligned} \tag{10}$$

The N-I transition entropy is given by

$$\begin{aligned} \Delta\Sigma c = Nk\Bigg\{ & \frac{x^2}{2}\left(\Gamma_c^{RR} - \frac{5L_R}{4D_R} c_R\right) S_R^2 + \frac{(1-x)^2}{2}\left(\Gamma_c^{DD} - \frac{5\pi D_D}{16 L_D} c_D\right) S_D^2 \\ & + P_2(\hat{n}_R \cdot \hat{n}_D) x(1-x)\left(\Gamma_c^{RD} + \frac{5D_D}{8D_R}\sqrt{\frac{L_R}{L_D}}\sqrt{c_R c_D}\right) S_R S_D \Bigg\} \end{aligned} \tag{11}$$

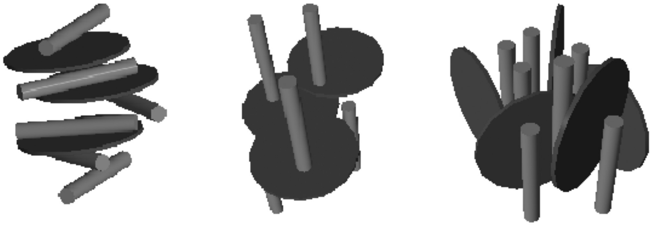
Further we can find the N-I transition temperature from condition $F_{nem} = 0$ for S_R, S_D is not 0.

CALCULATION AND RESULTS

We investigate the following four types of structure shown in Figure 1: N^+ (Fig. 1(c)), N^- (Fig. 1(a)) and N_X (Fig. 1(b)) are the uniaxial nematic phases in which two directors n_R and n_D are parallel, and Figure 1(d) shows the biaxial nematic phase, say Nb, in which n_R and n_D are perpendicular to each other.

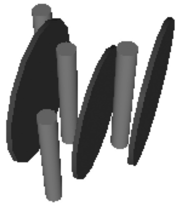
In Figure 2, for example, we show the free energy as a function of composition at T = 100 K. Though the free energy of the Nb phase is lower than the uniaxial nematic phases near $x_R = 0.5$, the coexistent phase of N^+ and N^- has lower energy than it. The state N_X of Figure 1(b) cannot be found as a stable solution of Eq. (9).

Figure 3 shows the T vs x phase diagram of this system. Figure 3a is for numerical parameters:



(a)$S_R<0$, $S_D>0$ (N^-) (b)$S_R>0$,$S_D>0$ (N_X) (c)$S_R>0$, $S_D<0$ (N^+)

$n_R \parallel n_D$(uniaxial nematic)



(d)$n_R \perp n_D$ (biaxial nematic) (Nb)

FIGURE 1 Nematic structures for rod-disc mixture.

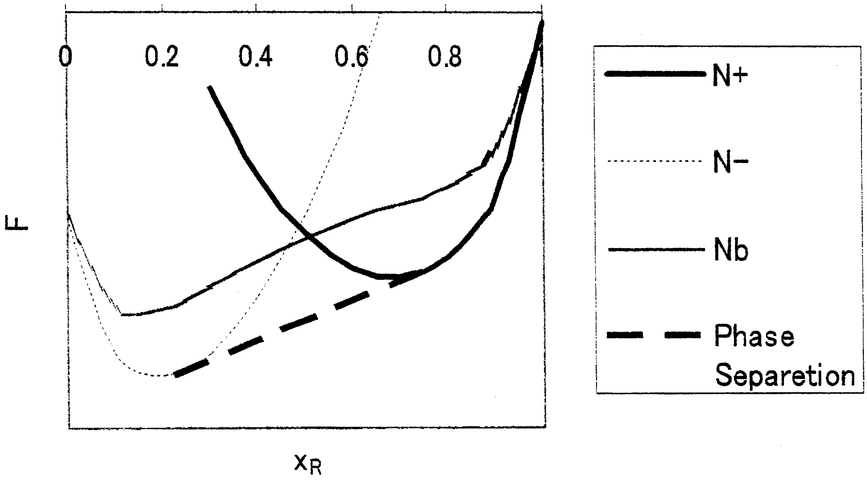


FIGURE 2 Free energy for T = 100 K.

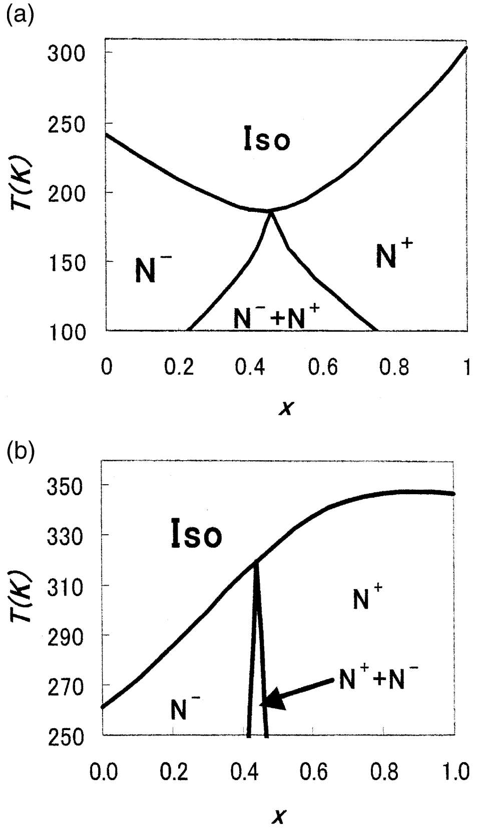


FIGURE 3 (a). The phase diagram for each anisotropy are 5. (b). The phase diagram for each anisotropy are 20.

$$L_R = 25, \quad D_R = 5, \quad \tilde{A}^{RR}/k = 622, \quad \tilde{C}^{DD}/k = 1000, \quad c_R = 0.4$$
$$L_D = 5, \quad D_D = 25, \quad \tilde{A}^{DD}/k = 622, \quad \tilde{C}^{DD}/k = 1000, \quad c_D = 0.4$$
$$\tilde{A}^{RD} = -0.5\sqrt{\tilde{A}^{RR} \cdot \tilde{A}^{DD}}, \quad \tilde{C}^{RD} = \sqrt{\tilde{C}^{RR} \cdot \tilde{C}^{DD}}$$

and Figure 3b is for,

$$L_R = 20^{4/3}, \quad D_R = 20^{1/3}, \quad \tilde{A}^{RR}/k = 622, \quad \tilde{C}^{DD}/k = 1000, \quad c_R = 0.11$$
$$L_D = 1, \quad D_D = 20, \quad \tilde{A}^{DD}/k = 622, \quad \tilde{C}^{DD}/k = 1000, \quad c_D = 0.11$$
$$\tilde{A}^{RD} = -\sqrt{\tilde{A}^{RR} \cdot \tilde{A}^{DD}}, \quad \tilde{C}^{RD} = \sqrt{\tilde{C}^{RR} \cdot \tilde{C}^{DD}}$$

Thus, we found that the stable phases in the mixtures are optically positive rod-like nematic phase (N^+) for $x > 0.5$, negative disc-like one (N^-) for $x < 0.5$ and the coexistence of N^+ and N^- phases near $x = 0.5$. And if aspect ratio is larger the coexistence region becomes narrower by comparing between Figure 3a and Figure 3b.

In Figure 4a, the order parameters are shown as the function of composition at $T = 220\,K$ for the system of Figure 3a. The N^--I first order phase transition by concentration change occurs about $x = 0.15$ and the N^+-I one about $x = 0.7$ in this case. We show in Figure 4b the temperature dependence of the order parameters for $x = 0.7$ for the system of

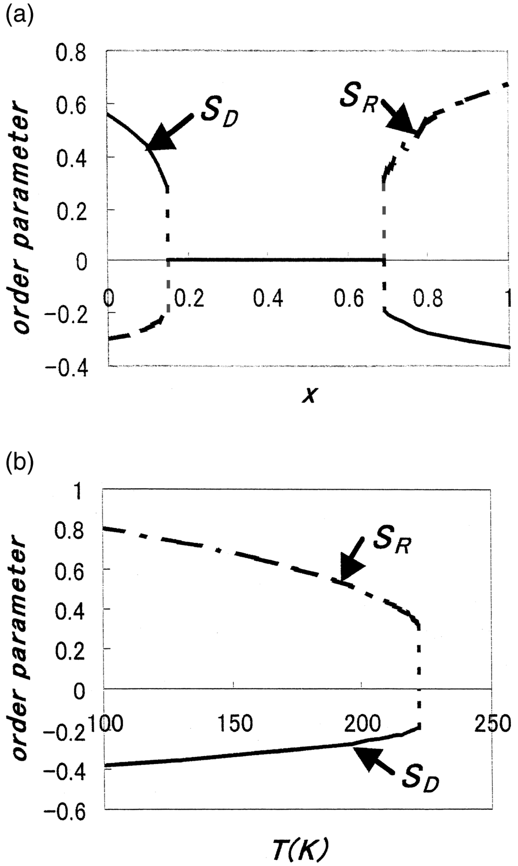


FIGURE 4 (a). Composition dependence of order parameter for Figure 2a and $T = 220\,K$. (b). Temperature dependence of order parameter for Figure 2a and $x = 0.7$.

Figure 3a, where the N^+-I first order phase transition occurs due to the temperature change.

In Figure 5, we show the effect on transition temperature and entropy of magnitude of interaction between different kind of molecules. We can see from Figure 5(a). If Γ^{DD} the interaction between different kinds of molecules becomes strong, the transition temperature increases. On the other hand, as shown in Figure 5(b), the transition entropy becomes lower when Γ^{DD} increases.

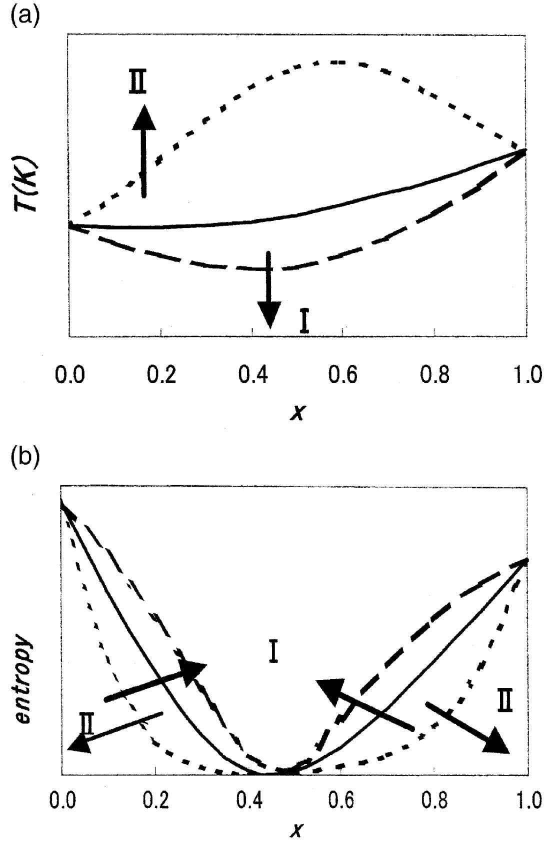


FIGURE 5 (a). Changing transition temperatures. (b) Changing transition entropies. Changes of transition temperatures(Fig. 4a) and entropies(Fig. 4b) when Γ^{RD} which the interaction between different kind of molecules changes. Case I: Weak coupling; Attractive interaction decreases or volume of rod-like molecules increases. Case II: Strong coupling; Attractive interaction increases or volume of disc-like molecules increases.

We examine the lyotropic system using only hard-core potential and show this result in Figure 6. It is for numerical parameters:

$$L_R = 20^{\frac{4}{3}} \quad D_R = 20^{\frac{1}{3}}$$
$$L_D = 1 \quad D_D = 20$$

Thus, biaxial nematic phase don't occur of this system as same as thermotropic phase transition. And this result predict that re-entrant phase transition occur by concentration in the mixture of rod-like and disc-like molecules.

CONCLUDING REMARKS

Assuming the intermolecular attraction as well as the hard-core repulsion, we found for mixtures of rod-like and disc-like molecules that the biaxial nematic phase is less stable than uniaxial phases. The first order thermotropic phase transitions occur between two types of uniaxial nematic, say N^+ and N^-, and isotropic phases. We can expect that the N^+ to N^- transition by changing the mixing ratio with a finite coexistence region. The uniaxial phases coexistence region get narrower when aspect ratios of rod and disc get larger at the same time. It is possible that the re-entrant phase transition occur for the lyotropic system.

The biaxial nematic phase Nb which has been predicted by computer simulation for very large aspect ratio such as 15 or 20 [1]. However our result indicate that Nb does not appear. We expect that the contradiction is due to the simplification of our model or simulation system size. Phase separation between N^+ and N^- might be taken for Nb phases, if the system

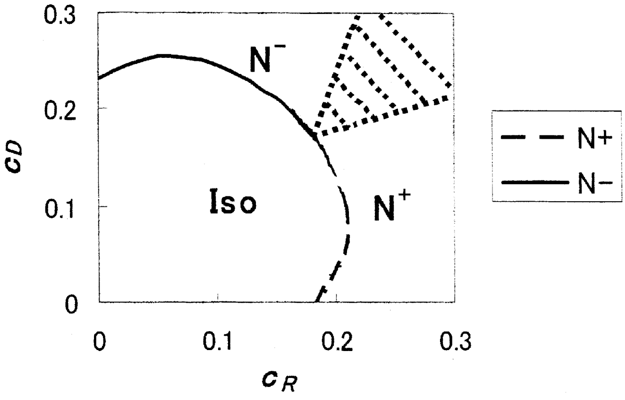


FIGURE 6 The phase diagram in the lyotropic system.

size of the simulation is small. Experiment in colloidal lyotropic system for which each aspect ratio are $L_R/D_R \sim 10$ and $D_D/L_D \sim 15$ could not find the biaxial nematic phase Nb [3]. And our results do not contradict experimental one of thermotropic system [4].

Though liquid crystalline property of mixture is complex, our present model and method can be applied to both the lyotropic and thermotropic systems. We shall further investigate for comprehensive understandings considering also the possibility of more ordered structures such as the smectic and columnar phases.

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