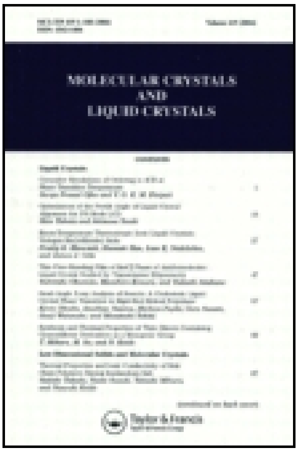

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Phase Behavior of Nematic-Nonnematic Binary Systems

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PHASE BEHAVIOR OF NEMATIC-NONNEMATIC BINARY SYSTEMS

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Abstract The effect of addition of several nonnematic solute to nematic liquid crystal 5CB was studied. We found the increase of nematic-isotropic phase transition temperature in ANB/5CB mixture,contrary to the usually observed depression. The results were analyzed by a mean field treatment of mixture.

INTRODUCTION

The addition of a non-mesomorphic solute to a nematic liquid crystal usually causes the depression of the phase transition temperature between the nematic-isotropic phases(T_{NI})[1]. The highness of T_{NI} has been often regarded as a measure of the purity of nematic liquid crystal. The addition also produces the appearance of a two phase region in which nematic and isotropic phases exist simultaneously over a temperature range of several degrees[1]. Physical properties of such mixtures, their dependence on solute size, shape and flexibility, have been studied extensively by means of various methods, including thermal and NMR measurement[1,2]. For such purpose, non-mesomorphic compounds such as alkane which has no specific interaction with nematic molecules are preferentially used as a solute. The effect of admixing other type of sulutes would be interesting if solutes are chosen on the reasonable ground. In this study, p-amino-p'-nitro-biphenyl(ANB) and p,p'-dinitro-biphenyl(DNB) were used as solutes to liquid crystalline 4-n-pentyl-4'-cyanobiphenyl (5CB) because of their structural similarity with the core part of 5CB molecule.

We found the addition of ANB to 5CB enhance the nematic-isotropic transition temperature (T_{NI}), contrary to the usually observed depression. The addition of DNB hardly change T_{NI}.

EXPERIMENT

ANB was synthesized by the partial reduction of DNB and purified by several recrystalization from ethanol[3]. Commercial 5CB was used without further purification. Transition temperature of ANB/5CB and DNB/5CB dilute mixtures was measured by using the hot stage under polarizing microscope and also by the differential scanning calorimetry.

RESULTS AND DISCUSSION

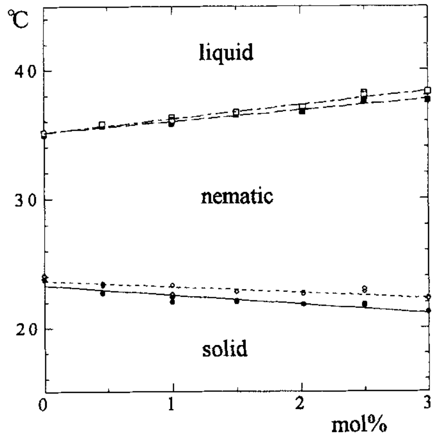

FIGURE 1a

Phase diagram of ANB-5CB system.

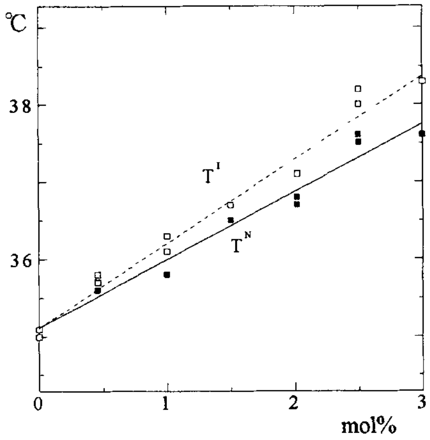

FIGURE 1b

T^N and T^I in ANB-5CB system.

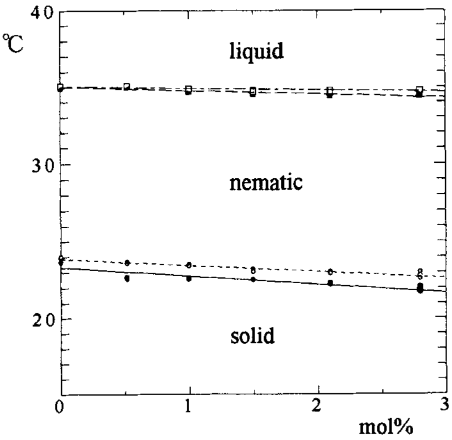

FIGURE 2a

Phase diagram of DNB-5CB.

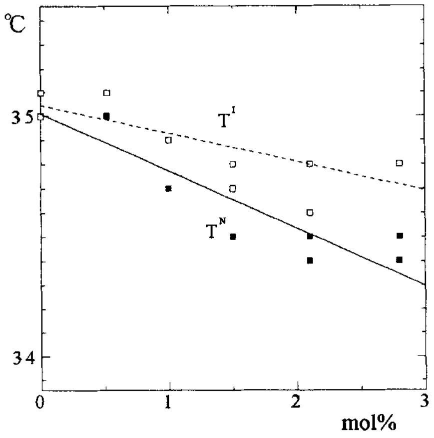

FIGURE 2b

T^N and T^I in DNB-5CB system.

Figure 1a shows the phase diagram of ANB/5CB system, and in Figure 1b the nematic-isotropic transition region is enlarged. Both T^N and T^I increase with the concentration of ANB. The temperature range of two phase region considerably narrow compared with the case of alkane addition. The behavior shows that ANB is slightly more soluble in nematic phase than in isotropic liquid. Figure 2a and 2b shows the phase diagram of DNB/5CB system and its enlarged diagram. It is seen that the addition of DNB to 5CB causes merely little depression of T^N and T^I. The temperature range of two phase region is indiscernibly narrow. Note the vertical scale of Figure 2b. In Figure 3, the change of nematic isotropic temperature of ANB/5CB and DNB/5CB mixtures are shown together with that of tetracyanoethylene(TCNE)/5CB and 2,3-dimethylbutane/5CB mixtures which had been reported previously by one of authors[4]. As can be seen in Figure 3, behavior of transition temperature shows various trend depending on admixing solutes.

We investigated various behavior of T^N and T^I on the basis of a simple thermodynamic treatmen[4]. The chemical potential of a solvent(A) in the nematic phase (μ_A^N) is given as the sum of the orientational contribution ($\mu_A^{N,onen}$) and the non-orientational (or configurational) contribution ($\mu_A^{N,config}$)[7];

$$\mu_A^N\left(T,\phi_B,\langle P_{2,A}\rangle\right) = \mu_A^{N,onen}\left(T,\phi_B,\langle P_{2,A}\rangle\right) + \mu_A^{N,config}\left(T,\phi_B\right) \qquad (1)$$

where ϕ_B is the volume fraction of non-mesomorphic solute(B). The chemical potential of nematics in the isotropic phase is written as

$$\mu_A^I\left(T,\phi_B\right) = \mu_A^{I,config}\left(T,\phi_B\right) \qquad (2)$$

In the two phase region, the equiriblium condition is given by

$$\mu_A^N\left(T^N,\phi_B^N,\langle P_{2,A}\rangle\right) = \mu_A^{I,config}\left(T^N,\phi_B^I\right) \qquad (3)$$

For a given ϕ_B^N, the temperature T^N at which the two phases coexist is determined by the condition

$$\mu_A^{N,onen}\left(T^N,\phi_B^N,\langle P_{2,A}\rangle_{NI}\right) = 0 \qquad (4)$$

where $\langle P_{2,A}\rangle_{NI}$ is the critcal ordir parament of A.

The orientational part of the chemical potential was calculated on the basis of the mean field of Marcelja's theory[4,6]. The strength of the mean field exerted on a solvent nematic molecule (X_A) and on a solute molecule(X_B) are written as,

$$
\begin{aligned}
-X_A &= (1-\phi_B)\upsilon_{AA}\langle P_{2,A}\rangle + \phi_B\upsilon_{BA}\langle P_{2,B}\rangle \\
-X_B &= \phi_B\upsilon_{AB}\langle P_{2,A}\rangle
\end{aligned}
\qquad (5)
$$

where υ_{KL} represent the strength of orientational field from the component K to L. Then, the mean field potentials of A and B molecules are given by $X_A \cdot P_2(\cos\theta_A)$ and $X_B \cdot P_2(\cos\theta_B)$ respectively, where θ_A and θ_B are the angle between the director of nematics and the molecular long axis of A and B. $P_2(x)$ is the second order Legendre polynomial. The orientational part of the chemical potential is given, following usual treatmen[7], as

$$
\begin{aligned}
\mu_A^{N,orien} &= -\frac{1}{2}X_A \cdot \langle P_{2,A}\rangle - kT\ln Z_A \\
\mu_B^{N,onen} &= -\frac{1}{2}X_B \cdot \langle P_{2,B}\rangle - kT\ln Z_B
\end{aligned}
\qquad (6)
$$

Z_A is the orientational partition function of a A molecule, $Z_A = \int \exp\{X_A \cdot P_2(\cos\theta_A)/(kT)\}d\cos\theta_A$. Simple inspection shows that the chemical potential of nematics in a mixture is related to that of pure nematics as

$$
\mu_A^{N,onen}\left(\frac{X_A}{\upsilon_{AA}\langle P_{2,A}\rangle}\cdot T, X_A, \phi_B\right) = \frac{X_A}{\upsilon_{AA}\langle P_{2,A}\rangle}\cdot\mu_A^{N,orien}(T, \upsilon_{AA}\eta_A, 0) \qquad (7)
$$

For pure nematics which has nematic-isotropic transition temperature T_{NI}° and critical order parameter $\langle P_{2,A}\rangle_{NI}^{\circ}$, the orientational part of the chemical potential satisfies following relation,

$$
\mu_A^{N,onen}\left(T_{NI}^{\circ}, \upsilon_{AA}\langle P_{2,A}\rangle_{N,I}^{\circ}, 0\right) = 0 \qquad (8)
$$

Applying this to the right-hand side of Eq.(7), the following equation is easily obtained,

$$
\mu_A^{N,orien}\left((1-S)\phi_B T_{NI}^{\circ}, \phi_A\theta_{AA}\langle P_{2,A}\rangle_{NI} + \phi_B\theta_{BA}\langle P_{2,B}\rangle_{NI}, \phi_B\right) = 0 \qquad (9)
$$

$$
S = 1 - \frac{\upsilon_{BA}\langle P_{2,B}\rangle_{NI}}{\upsilon_{AA}\langle P_{2,A}\rangle_{NI}^{\circ}}. \qquad (10)
$$

Eq.(9) indicates the orientational chemical potential of nematics vanish at the temperature

$$\frac{T_N}{T_{NI}^\circ}=1-S\cdot\phi_B^N \tag{11}$$

The ϕ_B^I in Eq.(3) is estimated by the equation[1,5].

$$\frac{\Delta h_A^\circ}{R}\left(\frac{1}{T^N}-\frac{1}{T_{NI}^\circ}\right)=\frac{\gamma_A}{\gamma_B}\left(\phi_B^I-\phi_B^N\right).$$

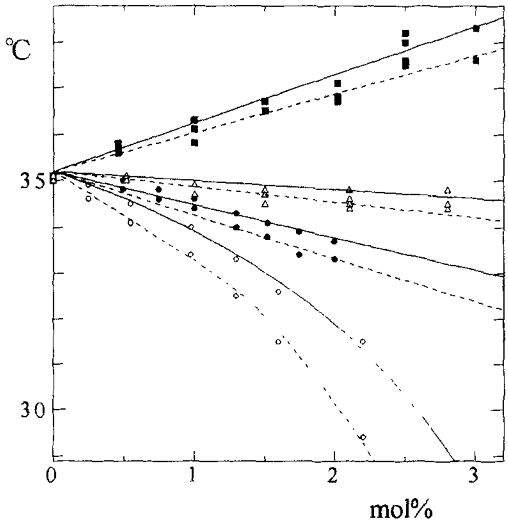

FIGURE 3

T^N and T^I in 5CB mixtures.

---○---○--- TCNE/5CB
---●---●--- DMB/5CB
---△---△--- DNB/5CB
---■---■--- ANB/5CB

$\langle P_{2,A}\rangle$ of ANB in 5CB measured by various methods do not differ much compared with $\langle P_2\rangle$ of host 5CB, and we can expect $\langle P_{2,A}\rangle_{NI}^\circ\sim\langle P_{2,B}\rangle_{NI}$ in Eq.(10). The enhancement of phase transition temperature T^N with the addition of ANB indicates $\upsilon_{BA}>\upsilon_{AA}$; the strength of orientatinal field exerted on 5CB molecule by ANB is stronger than that of 5CB molecule. ANB molecule is of approximately same size and shape with host 5CB and is very polar owing to the coexistence of π-electron donating(NH_2) and π-electron accepting(NO_2) groups in the same molecule. ANB seems to have high compatibility with 5CB and considerably strong anisotropic interaction. Hence, the relation $\upsilon_{BA}>\upsilon_{AA}$ would be reasonable.

DNB also has similar size and shape with 5CB like as ANB, and we can expect $\langle P_{2,A}\rangle_{NI}^{\circ} \sim \langle P_{2,B}\rangle_{NI}^{\circ}$ in Eq.(10). The behavior of T^N of DNB/5CB system in Figure 2 indicates $\upsilon_{AA} \sim \upsilon_{BA}$. DNB is non-polar by symmetry. The relation $\upsilon_{AA} \sim \upsilon_{BA}$ indicates that dominant anisotropic orientational interaction is caused by that of non-polar core parts. The difference between ANB/5CB and DNB/5CB system, then, would be ascribed to the additional role of dipole-dipole interaction. The behavior of TCNE/5CB and DMB/5CB system had been analyzed in ref. 4.

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