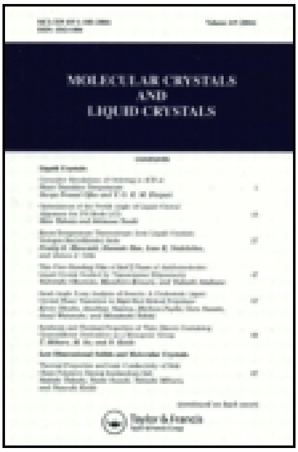

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Phase Behavior of Nematic-Nonnematic Binary Systems-Effects of Hydrogen Bonding-

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PHASE BEHAVIOR OF NEMATIC-NONNEMATIC BINARY SYSTEMS – EFFECTS OF HYDROGEN BONDING –

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Abstract Binary mixtures of nematic 5CB with some kind of non-mesomorphic solutes were found to cause the increase in nematic-isotropic transition temperature, contrary to usually observed decrease. "Unusual" solutes found in this work all had active hydrogen which can act as hydrogen bond donor. Admixing of methyl or ethyl substituted compounds of above solutes resulted in usual depression of transition temperature. "Unusual" increase in clearing temperature were attributed to the hydrogen bonding interaction between 5CB and solutes. The thermal effects of hydrogen bonding interaction between 5CB and various non-mesomorphic solutes were studied in detail.

INTRODUCTION

The study of binary systems consist of non-mesomorphic solute and mesomorphic solvent is of fundamental importance. Many extensive theoretical and experimental investigations have been carried out and reported[1,2]. The admixing of non-mesomorphic solute to nematics usually causes the lowering of nematic-isotropic phase transition temperature(T_{NI}), and the appearance of the two-phase region. But several unusual cases, in which addition of non-mesomorphic impurities leads to the elevation of transition temperature, were known to exist[3,4].

In a previous paper[4], we reported that the addition of non-mesomorphic 4-amino-4'-nitrobiphenyl (ANB) to nematic 4-pentyl-4'-cyanobiphenyl (5CB) resulted in the increase of transition temperature, contrary to usually observed depression. This unusual behavior had been ascribed to the high polarity of ANB molecule.

In this work, we carried out further investigation to clarify the origin of these unusual behavior. We found the addition of non-mesomorphic solutes;

benzenecarboxylic acid (benzoic acid); (BCA),
p-biphenylcarboxylic acid; (pBiCA),
p-hydroxybiphenyl; (pBiOH),
p,p'-dihydroxybiphenyl; (p,p'BiOH),

to 5CB resulted in the elevation of nematic-isotropic transition temperature, whereas their methyl or ethyl derivatives of above solutes all showed usual depression of transition temperature T_{NI}. These observation indicate clearly that unusual elevation of nematic-isotropic transition temperature is caused by the formation of hydrogen bond between nematic 5CB and non-mesomorphic solutes.

EXPERIMENT

Commercial 5CB (Tokyo Kasei) was used without further purification. Methyl ester of p-biphenylcarboxylic acid was synthesized by the usual Fischer-Speier method from p-biphenylcarboxylic acid and methanol, and purified by several recrystallization from ethanol. Other non-mesomorphic solutes were purchased and used without further purification. The nematic-isotropic transition temperature was measured under polarizing microscope using a hot stage.

RESULTS AND DISCUSSION

Fig.1(a) shows that the addition of benzenecarboxylic acid (BCA) to 5CB increases the nematic-isotropic transition temperature(T_{NI}). Whereas, as shown in Fig.1(b), the addition of its methyl ester which hardly has H-bond donating power result in usual decrease of T_{NI}. Similar but more marked increase of T_{NI} was observed in pBiCA/5CB binary system, as shown in Fig.2(a), while the admixing its methyl ester caused normal depression of T_{NI} (Fig.2(b)). In these and following figures, T_N denote the temperature at which isotropic phase begin to appear in nematics on heating, T_I the temperature at which nematic phase disappear completely.

These observation strongly indicates that the unusual increase in T_{NI} is ascribed to the hydrogen bond formation between cyano group of 5CB and OH of carboxylic group in BCA and pBiCA, although the hydrogen accepting power of cyano group is known usually to be rather weak.

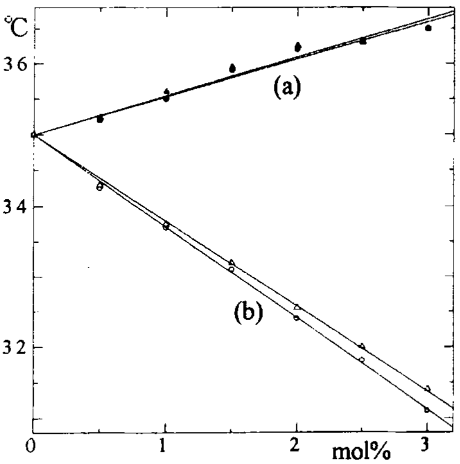

FIGURE1 : Phase diagram of

(a) BCA/5CB system (●: T_N, ▲: T_I)

(b) BCA methyl ester/5CB system (○: T_N, △: T_I)

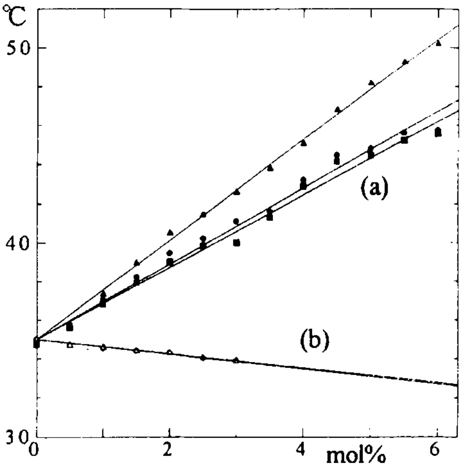

FIGURE2 : Phase diagram of

(a) pBiCA/5CB system (■: T_N, ●: $T_{I'}$, ▲: T_I)

(b) pBiCA methyl ester/5CB system (○: T_N, △: T_I')

Recently, many investigations on the formation of mesomorphic phases through intermolecular hydrogen bonding interactions were reported^{5,6}. Most typical combination of functional groups of H-bond donor and acceptor was carboxylic OH group and nitrogen in pyridyl or dipyridyl moiety. Thermal stability of these H-bonded mesophases were usually surprisingly high, indicating the presence of considerably strong H-bonding in the systems. These unusual thermal stability of H-bonded mesophases was interpreted as the indication that hydrogen bondings are much stronger in the orientational field of liquid crystalline state than in non-orienting isotropic solution. We believe that similar mechanism which makes the hydrogen bonding stronger is working also in our case. It is noted that the rate of rise in T_{NI} with solute concentration is about twice larger for pBiCA/5CB than for BCA/5CB system. This implies that the hydrogen-bonded complex takes preferentially elongated conformation by virtue of orienting field of liquid crystalline state. The length to diameter ratio is larger in 5CB-pBiCA complex than 5CB-BCA complex, which leads to more stabilization of nematic state for pBiCA than for BCA.

Furthermore, in the case of pBiCA/5CB binary system, a peculiar phase transition behavior which does not occur for other solutes studied in this work was observed. This binary system seems to have two kind of coexisting region; one is between T_N and $T_{I'}$ and another is between $T_{I'}$ and T_I in Fig.2(a). This behavior is now under investigation.

Fig.3 shows the phase behavior of p-hydroxybiphenyl(pBiOH)/5CB and p,p'-dihydroxybiphenyl(p,p'BiOH)/5CB binary systems, respectively. Both solutes lead to the increase of T_{NI}. The rate of increase of T_{NI} with solute concentration is about four times larger for pBiCA than for pBiOH, indicating that carboxylic OH is stronger hydrogen bond donor than hydroxy OH. The stronger H-bond donating power of carboxylic group over hydroxy group was also confirmed by the observation that BCA lead to the rising of T_{NI}, whereas the addition of phenol lowered T_{NI}. Because aromatic carboxylic acid and corresponding hydroxy compound give H-bonded complex of similar size and shape, the difference of the two binary systems may be attributed to the difference in the amount of H-bonded complexes in both systems.

To investigate the effect of shape of H-bonded complex, we carried out the measurement on o-hydroxybiphenyl(oBiOH)/5CB and o,o'-dihydroxybiphenyl (o,o'BiOH)/5CB binary systems. Compared with p-hydroxy compound, these solutes produce some more bulky H-bond complexes. These solutes resulted in decrease of T_{NI} as shown in Fig.4. These results indicate the importance of the shape of H-bonded complex in phase behavior of binary system.

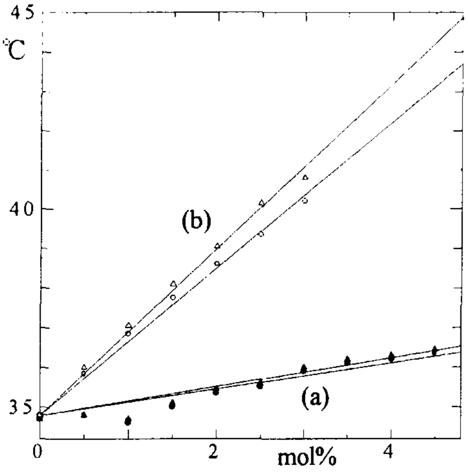

FIGURE3 : Phase diagram of
(a) pBiOH/5CB system (●: T_N, ▲: T_I)
(b) p,p'BiOH/5CB system (○: T_N, △: T_I)

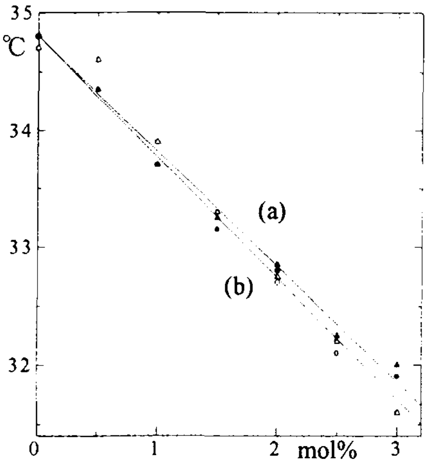

FIGURE4 : Phase diagram of
(a) oBiOH/5CB system (●: T_N, ▲: T_I)
(b) o,o'BiOH/5CB system (○: T_N, △: T_I)

In Fig.5 and 6, results are summarized for several nonmesomorphic solute /5CB binary systems to show more clearly that the rate of increase or decrease in T_{NI} by solute admixing varies rather widely depending on natures of solute.

In this work, solute concentration was limited to a rather low level owing to poor solubility of solute. Study of other combination of solute and liquid crystalline solvent which have strong power of H-bonding interaction and high mixing capacity would be a interesting subject to improve and control characteristics of liquid crystals.

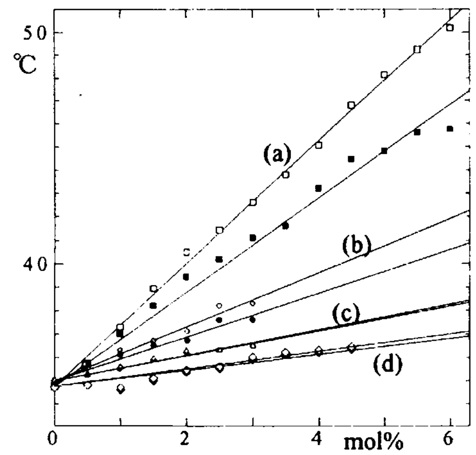

FIGURE5 : Phase diagram of

(a) pBiCA/5CB (■: T_N,□: T_I)

(b) p-amino p'-nitrobiphenyl/5CB (●: T_N,○: T_I)

(c) BCA/5CB (▲: T_N,△: T_I)

(d) pBiOH/5CB (◆: T_N,◇: T_I)

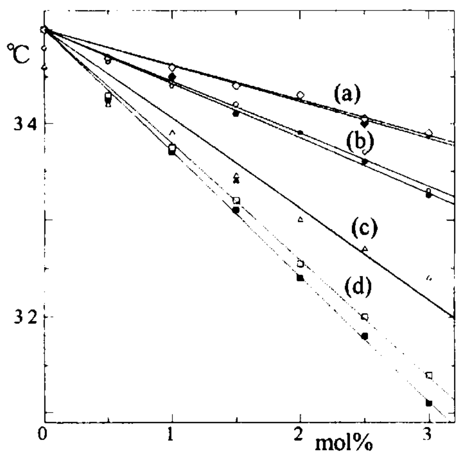

FIGURE6 : Phase diagram of

(a) m-aminobiphenyl/5CB (◆: T_N,◇: T_I)

(b) pBiCA methyl ester/5CB (●: T_N,○: T_I)

(c) p-pentylbiphenyl/5CB (▲: T_N,△: T_I)

(d) methyl benzoate/5CB (■: T_N,□: T_I)

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