Thermal Stability Enhancement of Liquid-crystal Phase by Charge-transfer Interaction in Binary Mixtures. Application of Solid-solution Model

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Synopsis. Phase transition in liquid crystal of binary mixture consisting of electron donor and acceptor was examined by using modified solid-solution model. The charge-transfer interaction between donor and acceptor is essential for parallel molecular arrangement in liquid crystal, resulting in thermal stability enhancement of mesophase in binary mixture.

Much attention has been paid to a great number of liquid crystals, which show intermediate state between crystalline solid and isotropic liquid.[1] Intermolecular attractions appear to be essential for producing the parallel molecular arrangement characteristic of such a state. Binary systems have been often used to achieve extended liquid crystalline temperature ranges.[2,3] Usually, the mesophase→isotropic liquid transition temperature of binary mixture varies linearly with composition. However, large deviations from such a linearity are observable, if molecular complex formation takes place between the components of the binary system. Complex formation due to electron donor-acceptor (charge-transfer) interaction may be effective for parallel molecular arrangement in liquid crystals. Park *et al.* examined nematic phase→isotropic liquid transition temperature (T_{NI}) in the binary system of *N*-(*p*-methoxybenzylidene)-*p*-*n*-butylaniline (MBBA) and 4-cyano-4′-pentylbiphenyl (CPB) and in several closely related binary mixtures, because there was a possibility of a weak charge-transfer interaction between a donor of MBBA and an acceptor of CPB.[2] As is shown in (a) of Fig. 1, the experimental relation of T_{NI} to composition of MBBA–CPB mixtures exhibits a broad curve whose maximum is located near 1:1 mole ratio, and T_{NI} of mixture is higher than the straight line joining T_{NI} of the two components ((c) of Fig. 1). In the present paper, using modified solid-solution model, we shall show that the attractive forces between donor and acceptor due to charge-transfer interaction is essential for such a thermal stability enhancement of liquid-crystal phase.

In the following, we discuss nematic phase induced by charge-transfer interaction in binary mixtures composed of rod-like donors and acceptors. Let us denote mole fractions of donors and acceptors as x_{D} and x_{A}, ($x_{\mathrm{D}}+x_{\mathrm{A}}=1$), respectively. The nematic→isotropic transition temperatures of pure donor and acceptor components are indicated by T_{D} and T_{A}, respectively. In general, nematic phase has a high degree of long range orientational order of the molecules, but no long range translational order. The molecules are spontaneously oriented with their long axes approximately parallel. In the present paper, we only consider how Gibbs free energy of nematic phase is influenced by the manner of mixing of donors and acceptors. For this purpose, we examine a three-dimensional lattice where molecules are oriented with their long axes parallel. It is assumed that such a lattice can be subdivided into two sublattices D and A, and that one site of D or A sublattice is surrounded by *z* equivalent nearest neighbor sites of A or D sublattice, respectively. Then, if the charge-transfer interaction between donor and acceptor is essential for parallel molecular arrangement to induce nematic phase, the nematic→isotropic phase transition should correspond to order→disorder phase transition for mixing of donors and acceptors. In other words, if the order of molecular arrangement of donors and acceptors remains, the system is supposed to be in nematic phase, while if the order is lost, it goes to isotropic liquid.

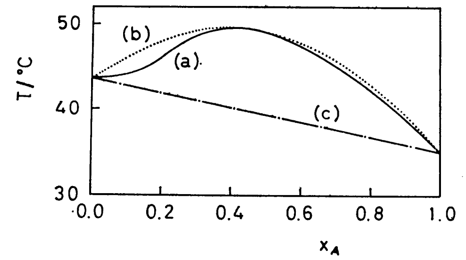

Fig. 1. Phase transition temperature of binary system of *N*-(*p*-methoxybenzylidene)-*p*-*n*-butylaniline (MBBA) and 4-cyano-4′-pentylbiphenyl (CPB). (a) indicates the experimental relation of nematic→isotropic transition temperature (T_{NI}) to mole fraction of CPB (x_{A}), as given by Ref. 2; (b), the theoretical relation of order→disorder transition temperature (T_{c}) to x_{A}; (c), the straight line joining T_{NI} of the two components. See text.

In order to show this situation more clearly, we take an approach of solid-solution model. Let us denote the numbers of sites of D and A sublattices as $N/2$ and $N/2$, respectively. The total number of donor and acceptor molecules in binary mixture is N, so that each site of D and A sublattices is occupied by either donor or acceptor. It is assumed that charge-transfer interaction acts in (1:1) manner between nearest neighbor donor and acceptor. In the system of pure donors ($x_{\mathrm{D}}=1.00$), all the sites of D and A sublattices are occupied by donors at temperature T_{D}, while in the system of pure acceptors ($x_{\mathrm{A}}=1.00$), by acceptors at temperature T_{A}. For binary mixtures, let us denote the numbers of donors and acceptors in D sublattice as $[^{\mathrm{d}}_{\mathrm{D}}]$ and $[^{\mathrm{a}}_{\mathrm{D}}]$, respectively, while the numbers of donors and acceptors in A sublattice as $[^{\mathrm{d}}_{\mathrm{A}}]$ and $[^{\mathrm{a}}_{\mathrm{A}}]$, respectively. We introduce order parameter X, ($0 \leq X \leq 1$), in such a way that, if $0 \leq x_{\mathrm{D}} \leq 1/2$, $[^{\mathrm{d}}_{\mathrm{D}}]=(1/2)N\ x_{\mathrm{D}}(1+X)$, $[^{\mathrm{a}}_{\mathrm{D}}]=(1/2)N\ (x_{\mathrm{A}}-x_{\mathrm{D}}X)$, $[^{\mathrm{d}}_{\mathrm{A}}]=(1/2)N\ x_{\mathrm{D}}(1-X)$ and $[^{\mathrm{a}}_{\mathrm{A}}]=(1/2)N\ (x_{\mathrm{A}}+x_{\mathrm{D}}X)$. In other words, if $X=1$, all donors occupy sites of D sublattice, while if $X=0$, donors and acceptors occupy sites of D and A sublattices randomly. Similar expressions can be obtained in the case of $0 \leq x_{\mathrm{A}} \leq 1/2$. The state of $X=0$ is called disordered phase with respect to mixing of donors and acceptors, while $X=1$, ordered phase. For order parameter X, the entropy for mixing donors and acceptors in binary mixture with composition (x_D, x_A) is then calculated as

$$
\begin{aligned}
S &= k \ln \frac{\frac{N}{2}!}{[\genfrac{}{}{0pt}{}{d}{D}]![\genfrac{}{}{0pt}{}{a}{D}]!} \frac{\frac{N}{2}!}{[\genfrac{}{}{0pt}{}{d}{A}]![\genfrac{}{}{0pt}{}{a}{A}]!} \\
&= -\frac{N}{2}k\{x_D(1+X)\ln x_D(1+X) \\
&\quad +(x_A-x_DX)\ln(x_A-x_DX)+x_D(1-X)\ln x_D(1-X) \\
&\quad +(x_A+x_DX)\ln(x_A+x_DX)\}. \qquad (1)
\end{aligned}
$$

Next, we examine the energy of our binary system in terms of order parameter X. We take only into consideration the intermolecular interaction energies between nearest neighbor molecules. The terms v_{DD}, v_{AA} and v_{DA} indicate the energies between a pair of donor-donor, acceptor-acceptor and donor-acceptor molecules in nearest neighbor sites, respectively. Note that v_{DD} and v_{AA} are weak stabilization energies due to van der Waals forces, while v_{DA} corresponds to stabilization energy due to charge-transfer interaction which is much stronger than v_{DD} and v_{AA}. Then, $v=(1/2)(v_{DD}+v_{AA})-v_{DA}\geq 0$. In terms of v, the energy, E, of binary mixture is given by

$$E = \frac{z}{2}N\{v_{DD}x_D{}^2+2v_{DA}x_Dx_A+v_{AA}x_A{}^2\} - zNx_D{}^2vX^2. \qquad (2)$$

For binary mixture, because of strongly attractive charge-transfer interaction, the order parameter at temperature $x_DT_D+x_AT_A$ is assumed to be $X=1$. If there is no volume change, Gibbs free energy of the system is given by

$$G_0 = E_0 - (x_DT_D+x_AT_A)S_0, \qquad (3)$$

where $E_0=zNv_{DA}x_D+(z/2)Nv_{AA}(x_A{}^2-x_D{}^2)$ and $S_0=-(Nk/2)\{2x_D \ln 2x_D+(x_A-x_D) \ln (x_A-x_D)\}$. At temperatures above $x_DT_D+x_AT_A$, we are only concerned with how Gibbs free energy is changed by the manner of mixing of donors and acceptors. For this purpose, we consider G_0 at temperature $x_DT_D+x_AT_A$ as a standard. When temperature is elevated from $x_DT_D+x_AT_A$, the order parameter decreases from $X=1$, and at certain temperature $T>x_DT_D+x_AT_A$, the energy and the entropy of our system change from E_0 and S_0 to E and S with order parameter $1>X\geq 0$, as are given by Eqs. 2 and 1, respectively. As long as we consider the effect of mixing upon free energy change, we can only discuss the difference of Gibbs free energy, ΔG, with respect to G_0, so that we obtain, at $T\geq x_DT_D+x_AT_A$,

$$\Delta G = E - E_0 - (T-x_DT_D-x_AT_A)\cdot(S-S_0). \qquad (4)$$

Eq. 4 means that, if temperature increases further, the order parameter decreases progressively, and at critical temperature T_c, the system undergoes a phase transition from ordered state with $X\neq 0$ to disordered state with $X=0$. In order to examine this condition, we consider $(\partial\Delta G/\partial X)=0$. The equation to determine X is given by

$$\frac{zx_Dv}{k(T-x_DT_D-x_AT_A)}X = \frac{1}{4}\ln\left(\frac{1+X}{1-X}\cdot\frac{x_A+x_DX}{x_A-x_DX}\right). \qquad (5)$$

After some manipulation of Eq. 5, the transition temperature is found to be $T_c=x_DT_D+x_AT_A+4x_Dx_AT_c{}^\circ$, where $T_c{}^\circ=zv/2k$. The magnitude of the thermal stability enhancement of ordered phase, $4x_Dx_AT_c{}^\circ$, above temperature $x_DT_D+x_AT_A$ is closely related to that of $v=(1/2)(v_{DD}+v_{AA})-v_{DA}\geq 0$. If $v=0$, then $T_c{}^\circ=0$, $T_c=x_DT_D+x_AT_A$ and we obtain no thermal stability enhancement of ordered state. However, if greater energy stabilization of v_{DA} occurs with parallel molecular arrangement of donors and acceptors, both v and $T_c{}^\circ$ increase appreciably and the stability enhancement of ordered state occurs accordingly.

Let us examine how the order→disorder phase transition for mixing of donors and acceptors corresponds to the nematic→isotropic phase transition of MBBA–CPB mixtures reported by Park *et al.*[2] If we take $T_D=43.5$ °C, $T_A=35.0$ °C, and $T_c{}^\circ=9.6$ °C, the order→disorder transition temperature $T_c=x_DT_D+x_AT_A+4x_Dx_AT_c{}^\circ$ *versus* composition is given by curve (b) of Fig. 1. This is compared with curve (a) of the experimental relation of T_{NI} to composition. In the composition range $0.4\leq x_A\leq 1.0$, both curves are found to agree quite well. The maximum temperature of T_c occurs at $x_A=0.39$, while that of T_{NI}, at $x_A=0.40$, so that the agreement of both values is very good. In the range $0.0\leq x_A\leq 0.4$, T_c is found to be somewhat higher than T_{NI}. This discrepancy implies that, in the range $0.0\leq x_A\leq 0.4$, some specific intermolecular interaction may take place in MBBA and CPB, so that our solid-solution model is not enough to describe that situation exactly. Except for this little discrepancy, the relation of T_c to composition appears to agree well with that of T_{NI} to composition. Therefore, the order→disorder transition for mixing of donors and acceptors corresponds well to the nematic→isotropic phase transition in MBBA–CPB mixtures. This means that the charge-transfer interaction between donor of MBBA and acceptor of CPB is essential for parallel molecular arrangement to induce nematic phase above temperature $x_DT_D+x_AT_A$. From the value of $T_c{}^\circ=9.6$ °C together with $T_c{}^\circ=zv/2k$, the magnitude of zv in the nematic phase of MBBA–CPB mixture is estimated to be 0.16 kJ mol^{-1}.

Finally, we have to say a few words about our solid-solution model. As was mentioned, nematic phase has a high degree of long range orientational order of the molecules but no long range translational order, whereas in solid-solution model, we consider a three-dimensional lattice where not only orientational order but also translational order are assumed. In the present paper, however, we have only discussed how Gibbs free energy of binary mixture is changed by the manner of mixing of donors and acceptors. As long as the problem is limited to such a difference in the degree of mixing, the solid-solution model is still applicable to liquid crystals where long range translational order no longer exists.

References

1) See, for example, S. Chandrasekhar, "Liquid crystals," Cambridge University Press, London, New York, New Rochelle, Melbourne, Sydney (1980).

2) J. W. Park, C. S. Bak, and M. M. Labes, *J. Am. Chem. Soc.*, **97**, 4398 (1975).

3) A. C. Griffin, R. F. Fisher, and S. J. Havens, *J. Am. Chem. Soc.*, **100**, 6329 (1978); M. Domon and J. Billard, *J. Phys. (Paris), Colloq.*, **40**, C3-413 (1979); N. K. Sharma, G. Pelzl, D. Demus, and W. Weissflog, *Z. Phys. Chem. (Leipzig)*, **261**, 579 (1980); K. Araya and Y. Matsunaga, *Bull. Chem. Soc. Jpn.*, **53**, 3079 (1980).