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Order-Disorder Transition in Nematic Liquid Crystalline Mixtures†

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The Pople-Karasz theory of order-disorder transition is extended from single- to multi-component mixtures of symmetric, rod-like molecules. A set of equations which determine the orientational and the positional order parameters of all components are derived. Thermodynamic quantities such as the pressure and the entropy of the mixtures are obtained as functions of the volume, the temperature and the mole fractions of the components.

This theory is applied to investigations of binary mixtures of nematogens. It is shown that the phase diagrams are strongly affected by the interaction energy between molecules of different kinds.

1 INTRODUCTION

In most cases the nematic liquid crystals which are applied to display devices are mixtures of more than two nematogens. Therefore, it is interesting and important not only from the viewpoint of fundamental studies on molecular interaction but also from the viewpoint of application to investigate the mole fraction dependence of the properties of multi-component mixtures.

Recently, orientational properties of dichroic dye molecules in nematic liquid crystals have been actively investigated in connection with application to

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guest-host type display devices. These types of mixtures, i.e., mixtures of nematogens and non-nematogens, also exhibit nematic phase.

Theoretical understanding of the multi-component orientational system seems to be not enough to date. Humphries, James and Luckhurst have extended the Maier-Saupe theory of the nematic mesophase to multi-component systems.[1] They have investigated the nematic-isotropic transition temperature of binary mixtures of nematogens and mixtures of a nematogen and a non-nematogen. Another approach is based on the lattice model.[2] Peterson, Martire and Cotter have studied a binary mixture of hard rods of different length.[3] This corresponds to a binary mixture of nematogens. Ågren and Martire have investigated a binary mixture of hard rods and hard cubes.[4] This corresponds to a binary mixture of a nematogen and a non-nematogen.

These two approaches take only the orientational order into account. Therefore, we can not discuss the solid-nematic transition properties by these approaches.

The simplest approach that contains both of orientational and positional order is the Pople-Karasz theory.[5] In the present paper, we will extend this theory from single- to multi-component mixtures of symmetric rod-like molecules in Section 2. The formulated equations will be applied to the investigation of binary mixtures of nematogens in Section 3. In Section 4, the limitations of this theory are discussed.

2 EXTENSION OF POPLE-KARASZ THEORY TO MULTI-COMPONENT MIXTURES

In this section, the Pople-Karasz theory of positional and orientational order-disorder transition is extended from single- to multi-component mixtures of symmetric, rod-like molecules.

Let us consider K-component molecular system. If the total number of molecules is n, the number of the I-th component is n_I and the mole fraction of the I-th component is c_I, we obtain

$$n_I = nc_I (I = 1,2, \ldots ,K) \tag{1}$$

where

$$\sum_{I=1}^{K} c_I = 1. \tag{2}$$

Following the method of Pople and Karasz, we can split the Helmholtz free energy A into two parts as

$$A = A' + A''. \tag{3}$$

The first part A' gives the contribution of the completely ordered system,

whereas the second part A'' gives the contribution due to the disordering of the positions and orientations of the molecules.

2.1 Calculation of A'

Lennard-Jones and Devonshire[6] derived the thermodynamic functions of a liquid (or dense gas) in terms of intermolecular forces using the cell model (or free volume theory). Wentorf *et al.*[7] developed this theory, calculated several thermodynamic quantities such as pv/nkT and compared theoretical results with experimental results on argon, nitrogen and hydrogen. Their calculation of A' was employed by Pople and Karasz.

Now, we must extend this theory (Lennard-Jones and Devonshire, Bentorf *et al.*) to multi-component systems. The extension is rather tedious but straightforward, so we describe the outline only briefly.

The interaction energy between an I-molecule and a J-molecule can be represented by the Lennard-Jones type potential:

$$\phi_{IJ}(r) = -4\epsilon_{0IJ}\left\{\left(\frac{r_{0IJ}}{r}\right)^6 - \left(\frac{r_{0IJ}}{r}\right)^{12}\right\}. \tag{4}$$

Here r is the separation of molecules, ϵ_{0IJ} is the maximum energy of interaction, and r_{0IJ} is the value of r for which $\phi_{IJ} = 0$.

If the number of nearest neighbors is z_1 and the distance between nearest neighbors is a, the averaged potential of an I-molecle within a cell can be written as

$$\psi_I(r) - \psi_I(0) = \sum_{J=1}^{K} z_1 c_J \epsilon_{0IJ}\left[\frac{v_{0IJ}^4}{v^4} L(y) - 2\frac{v_{0IJ}^2}{v^2} M(y)\right] \tag{5}$$

where r is the distance from the equilibrium position and $y = r^2/a^2$. In Eq. (5), we considered f.c.c. lattice and the total volume of the system, v, is equal to $na^3/\sqrt{2}$, and $v_{0IJ} = nr_{0IJ}^3$. In the nearest neighbor approximation (Lennard-Jones and Devonshire),

$$\begin{cases} L(y) = l(y), \\ M(y) = m(y), \end{cases} \tag{6}$$

and up to the third neighbor approximation (Bentorf *et al.*),

$$\begin{aligned} L(y) &= l(y) + \frac{1}{128} l\left(\frac{y}{2}\right) + \frac{2}{729} l\left(\frac{y}{3}\right), \\ M(y) &= m(y) + \frac{1}{16} m\left(\frac{y}{2}\right) + \frac{2}{27} m\left(\frac{y}{3}\right), \end{aligned} \tag{7}$$

where

$$\begin{cases} l(y) = (1 + 12y + 25.2y^2 + 12y^3 + y^4)(1 - y)^{-10} - 1, \\ m(y) = (1 + y)(1 - y)^{-4} - 1. \end{cases} \tag{8}$$

In the following calculation, we use Eq. (7).

The partition function of an I-molecule is given by

$$f_I(T) = (2\pi m_I kT)^{3/2} h^{-3} \int_0^{\epsilon a} 4\pi r^2 \exp\{-[\psi_I(r) - \psi_I(0)]/kT\} dr$$
$$= (2\pi m_I kT)^{3/2} h^{-3} 2\pi a^3 \int_0^{\epsilon'} y^{1/2} \exp\left\{ -\sum_{J=1}^{K} \frac{c_I \Lambda_{IJ}}{kT} \left[\left(\frac{v_{0IJ}}{v} \right)^4 L(y) - 2 \left(\frac{v_{0IJ}}{v} \right)^2 M(y) \right] \right\} dr \tag{9}$$

where m_I is the mass of an I-molecule, k is Boltzmann constant, h is Plank constant, $\Lambda_{IJ} = z_1 \epsilon_{0IJ}$ and

$$\epsilon = \left(\frac{3\sqrt{2}}{8\pi} \right)^{1/3} \simeq 0.55267.$$

The total energy when all molecules are at equilibrium positions is given by

$$E_0 = \frac{n}{2} \sum_{I,J} c_I c_J \psi_{IJ}(0) \tag{10}$$

where

$$\psi_{IJ}(0) = -\Lambda_{IJ} \left\{ p \left(\frac{v_{0IJ}}{v} \right)^2 - \frac{q}{2} \left(\frac{v_{0IJ}}{v} \right)^4 \right\}. \tag{11}$$

In Eq. (11), $p = q = 2$ when only nearest neighbor interactions are considered, and $p = 2.4090$, $q = 2.0219$ when other interactions are taken into account.

The partition function of the total system is

$$F(T) = \prod_{I=1}^{K} \{f_I(T)\}^{nc_I} \exp\left(-\frac{E_0}{kT} \right). \tag{12}$$

Then, the Helmholtz free energy is given by

$$\frac{A'}{nkT} = -\frac{1}{n} \ln F(T)$$
$$= -\sum_I c_I \ln f_I(T) + \frac{1}{2kT} \sum_{I,J} c_I c_J \psi_{IJ}(0) \tag{13}$$

where

$$\ln f_I(T) = \frac{3}{2}\ln\left(\frac{2\pi m_I kT}{h^2}\right) + \ln\left(2\pi\frac{\sqrt{2}\,\mathrm{v}}{n}\right) + \ln g_I \tag{14}$$

and

$$g_I = \int_0^{\epsilon} y^{1/2}\exp\left\{-\sum_{J=1}^{K}\frac{c_J\Lambda_{IJ}}{kT}\left[\left(\frac{\mathrm{v}_{0IJ}}{\mathrm{v}}\right)^4 L(y) - 2\left(\frac{\mathrm{v}_{0IJ}}{\mathrm{v}}\right)^2 M(y)\right]\right\}dy. \tag{15}$$

Equation (13) reduces to the Lennard-Jones and Devonshire's (or Bentorf *et al.*) equation for single-component system. It must be noted here that Eq. (13) [or Eq. (12)] does not contain the contribution of the entropy of mixing. This contribution will be included in A''.

2.2 Calculation of A''

Let us consider n normal α-sites and n interstitial β-sites. We suppose that the system is a solid state (at zero temperature) if all molecules occupy α-sites (or β-sites), and it is a liquid state if a half occupy α-sites and the other half occupy β-sites. Further, following the Pople and Karasz's model, we assume that the molecules take two kinds of orientational state 1 and 2 on each site. We suppose that the orientational order is perfect if all molecules are in 1-state (or 2-state) and there is no orientational order if a half are in 1-state and the other half are in 2-state. These two states must not be considered to correspond to up and down directions because in liquid crystals these two directions are equivalent. We regard these two states as two mutually perpendicular directions in the two-dimensional space. An extension of the treatment to more than two discrete orientations are possible[8] (for example, three mutually perpendicular orientations in the three-dimensional space), but we adopt the original Pople-Karasz's model for our preliminary study on mixtures.

After all, it is possible for each molecule to take four kinds of state, α_1, α_2, β_1 and β_2. Each α-site is supposed to be surrounded by z equivalent neighboring β-sites and each β-site by z α-sites. We also write z' for the number of α-sites (β-sites) closest to any given α-site (β-site).

We assume that there is a positional repulsive force between α-β neighbors and also an orientational repulsive force between α_1-α_2 neighbors or β_1-β_2 neighbors. Then, the interaction energy between neighboring molecules (one is an I-molecule on ξ-site in i-orientational state and the other is a J-molecule on η-site in j-orientational state) can be written as

$$W_{I\xi i:J\eta j} = W_{IJ}(1 - \delta_{\xi\eta}) + W'_{IJ}\delta_{\xi\eta}(1 - \delta_{ij}) \tag{16}$$

where W_{IJ} is the positional repulsive energy, W_{IJ} is the orientational repulsive

energy and

$$I,J = 1,2,\ldots,K$$
$$\xi,\eta = \alpha,\beta$$
$$i,j = 1,2.$$

Here, it must be noted that W_{IJ} and W'_{IJ} are not necessarily repulsive energies, that is, they are energy differences between unfavorable pairs and favorable pairs.

If $N_{I\xi i:J\eta j}$ is the number of neighboring pairs between $I\xi i$-molecules and $J\eta j$-molecules, the partition function of this system is given by

$$Z = F(T)\Omega(T)$$
$$\Omega(T) = \sum{}^{c} \exp[-\sum_{\substack{I,\xi,i \\ J,\eta,j}} W_{I\xi i:J\eta j} N_{I\xi i:J\eta j}/kT] \tag{17}$$

where $F(T)$ is the partition function of the completely ordered system obtained in section 2.1 and $\Omega(T)$ is the contribution due to disordering of the positions and orientations of the molecules. The symbol Σ^c means the summation over all configurations.

We can evaluate Ω by Bragg-Williams approximation. Let τ_I be the fraction of I-molecules on α-site and σ_I the fraction of I-molecules with 1-orientational state. Then, the number of I-molecules in ξi state, $n_{I\xi i}$, is given by

$$\begin{aligned} n_{I\alpha 1} &= n_I\tau_I\alpha_I, \\ n_{I\alpha 2} &= n_I\tau_I(1-\sigma_I), \\ n_{I\beta 1} &= n_I(1-\tau_I)\sigma_I, \\ n_{I\beta 2} &= n_I(1-\tau_I)(1-\sigma_I). \end{aligned} \tag{18}$$

The configurational partition function can be written as a sum of $\Omega(\{\tau_I\}, \{\sigma_I\})$, the partition functions for given $\{\tau_I\}$ and $\{\sigma_I\}$, as

$$\Omega = \sum_{\{\tau\}\{\sigma\}} \Omega(\{\tau_I\},\{\sigma_I\}) \tag{19}$$

where $\{\tau_I\}$ is the abbreviation of $\tau_1, \tau_2, \ldots, \tau_K$ and $\{\sigma_I\}\sigma_1, \sigma_2, \ldots, \sigma_K$. In Eq. (19), $\Omega(\{\tau_I\},\{\sigma_I\})$ is given by

$$\Omega(\{\tau_I\},\{\sigma_I\}) = \sum^{\{\tau_I\}\{\sigma_I\}} \exp\left[-\sum_{\substack{I,\xi,i \\ J,\eta,j}} W_{I\xi i:J\eta j} N_{I\xi i:J\eta j}/kT\right] \tag{20}$$

Where $\sum^{\{\tau_I\}\{\sigma_I\}}$ means the summation over the configurations for given $\{\tau_I\}$ and $\{\sigma_I\}$.

According to the Bragg-Williams approximation, we replace the exponent in Eq. (20) by its average value. Then, the summation reduces to the multiplication of $\gamma(\{\tau_I\},\{\sigma_I\})$, the number of terms for given $\{\tau_I\}$ and $\{\sigma_I\}$. Therefore, Eq. (20) reduces to

$$\Omega(\{\tau_I\},\{\sigma_I\}) = \gamma(\{\tau_I\},\{\sigma_I\}) \exp\left[-\sum_{\substack{I,\xi,i \\ J,\eta,j}} W_{I\xi i:J\eta j} \bar{N}_{I\xi i:J\eta j}/kT\right] \tag{21}$$

where $\bar{N}_{I\xi i;J\eta j}$ is the average number of $I\xi i$-$J\eta j$ neighbors for given $\{\tau_I\}$ and $\{\sigma_I\}$. In Eq. (21), $\gamma(\{\tau_I\},\{\sigma_I\})$ is given by

$$\gamma(\{\tau_I\},\{\sigma_I\}) = \left[\frac{n!}{\left(\sum_{I=1}^{K} n_I\tau_I\right)!\left\{\sum_{I=1}^{K} n_I(1-\tau_I)\right\}!}\right]^2 \times \frac{\left(\sum_{I=1}^{K} n_I\tau_I\right)!}{\prod_{I=1}^{K}[(n_I\tau_I\sigma_I)!\{n_I\tau_I(1-\sigma_I)\}!]} \times \frac{\left\{\sum_{I=1}^{K} n_I(1-\tau_I)\right\}}{\prod_{I=1}^{K}[\{n_I(1-\tau_I)\sigma_I\}!\{n_I(1-\tau_I)(1-\sigma_I)\}!]}. \quad (22)$$

As the pair interaction energy is given by Eq. (16), the exponent in Eq. (21) reduces to

$$-\frac{n}{2}\sum_{I,J}\left\{\frac{zW_{IJ}}{kT}c_Ic_J(\tau_I+\tau_J-2\tau_I\tau_J) + \frac{z'W'_{IJ}}{kT}c_Ic_J(2\tau_I\tau_J-\tau_I-\tau_J+1)(\sigma_I+\sigma_J-2\sigma_I\sigma_J)\right\}. \quad (23)$$

Substituting Eqs. (22) and (23) into Eq. (21) and using Stirling's theorem, we obtain

$$\omega(\{\tau_I\},\{\sigma_I\}) \equiv n^{-1}\ln\Omega(\{\tau_I\},\{\sigma_I\}) = -\sum_{I=1}^{K} c_I\ln c_I - \left(\sum_{I=1}^{K} c_I\tau_I\right)\ln\left(\sum_{I=1}^{K} c_I\tau_I\right) - \left\{\sum_{I=1}^{K} c_I(1-\tau_I)\right\}\ln\left\{\sum_{I=1}^{K} c_I(1-\tau_I)\right\} - \sum_{I=1}^{K} c_I\{\tau_I\ln\tau_I + (1-\tau_I)\ln(1-\tau_I) + \sigma_I\ln\sigma_I + (1-\sigma_I)\ln(1-\sigma_I)\} - \frac{1}{2}\sum_{I,J=1}^{K}\left\{\frac{zW_{IJ}}{kT}c_Ic_J(\tau_I+\tau_J-2\tau_I\tau_J) + \frac{z'W'_{IJ}}{kT}c_Ic_J(2\tau_I\tau_J-\tau_I-\tau_J+1)(\sigma_I+\sigma_J-2\sigma_I\sigma_J)\right\}. \quad (24)$$

Applying equilibrium condition,

$$\frac{\partial \omega}{\partial \tau_I} = \frac{\partial \omega}{\partial \sigma_I} = 0,$$

we obtain

$$\ln \frac{\tau_I \sum_{J=1}^{K} c_J \tau_J}{(1-\tau_I)(1-\sum_{J=1}^{K} c_J \tau_J)} = \sum_{J=1}^{K} \left\{ \frac{zW_{IJ}}{kT} + \frac{z'W'_{IJ}}{kT}(2\sigma_I\sigma_J - \sigma_I - \sigma_J) \right\} c_J(2\tau_J - 1), \quad (25)$$

$$\ln \frac{\sigma_I}{1-\sigma_I} = \sum_{J=1}^{K} \frac{z'W'_{IJ}}{kT} c_J(2\tau_I\tau_J - \tau_I - \tau_J + 1)(2\sigma_J - 1). \quad (26)$$

Equations (25) and (26) are $2K$ simultaneous equations of $2K$ unknowns, $\{\tau_I\}$ and $\{\sigma_I\}$. When $K = 1$ (single-component), they reduce to the equations obtained by Pople and Karasz.

Now, let us define the positional and orientational order parameters by

$$\begin{cases} Q_I \equiv 2\tau_I - 1, \\ S_I \equiv 2\sigma_I - 1. \end{cases} \quad (27)$$

Perfect order corresponds to $Q_I = S_I = 1$ and complete disorder to $Q_I = S_I = 0$. Substituting Eq. (27) into Eqs. (25) and (26), we obtain,

$$\ln \frac{(1+Q_I)(1+\sum_{J=1}^{K} c_J Q_J)}{(1-Q_I)(1-\sum_{J=1}^{K} c_J Q_J)} = \sum_{J=1}^{K} \left\{ \frac{zW_{IJ}}{kT} - \frac{z'W'_{IJ}}{2kT}(1 - S_I S_J) \right\} c_J Q_J, \quad (28)$$

$$\ln \frac{1+S_I}{1-S_I} = \sum_{J=1}^{K} \frac{z'W'_{IJ}}{2kT}(1 + Q_I Q_J) c_J S_J. \quad (29)$$

Apparently, $Q_I = S_I = 0$ ($I = 1, 2, \ldots, K$), i.e., isotropic liquid phase, is always a solution of Eqs. (28) and (29).

The nematic phase corresponds to $Q_I = 0$ and $S_I \neq 0$. Eq. (28) is always satisfied by $Q_I = 0$ ($I = 1, 2, \ldots, K$). Then, S_I is determined from

$$\ln \frac{1+S_I}{1-S_I} = \sum_{J=1}^{K} \frac{z'W'_{IJ}}{2kT} c_J S_J. \quad (30)$$

The plastic crystal phase corresponds to $S_I = 0$ and $Q_I \neq 0$. Eq. (29) is always satisfied by $S_I = 0$ ($I = 1,2, \ldots, K$). Then, Q_I is determined from

$$\ln \frac{(1 + Q_I)(1 + \sum_{J=1}^{K} c_J Q_J)}{(1 - Q_I)(1 - \sum_{J=1}^{K} c_J Q_J)} = \sum_{J=1}^{K} \left(\frac{zW_{IJ}}{kT} - \frac{z'W'_{IJ}}{2kT} \right) c_J Q_J. \tag{31}$$

The ordinary solid phase corresponds to $Q_I, S_I \neq 0$. Which phase is realized depends on which phase minimizes the Helmholtz free energy A'' given by

$$\begin{aligned}
\frac{A''}{nkT} = -\omega = -n^{-1} \ln \Omega &= \sum_{I=1}^{K} c_I \ln c_I \\
&+ \left\{ \sum_{I=1}^{K} \frac{c_I(1 + Q_I)}{2} \right\} \ln \left\{ \sum_{I=1}^{K} \frac{c_I(1 + Q_I)}{2} \right\} \\
&+ \left\{ \sum_{I=1}^{K} \frac{c_I(1 - Q_I)}{2} \right\} \ln \left\{ \sum_{I=1}^{K} \frac{c_I(1 - Q_I)}{2} \right\} + \sum_{I=1}^{K} c_I \left\{ \frac{1 + Q_I}{2} \ln \frac{1 + Q_I}{2} \right. \\
&+ \left. \frac{1 - Q_I}{2} \ln \frac{1 - Q_I}{2} + \frac{1 + S_I}{2} \ln \frac{1 + S_I}{2} + \frac{1 - S_I}{2} \ln \frac{1 - S_I}{2} \right\} \\
&+ \frac{1}{4} \sum_{I,J=1}^{K} \left\{ \frac{zW_{IJ}}{kT} c_I c_J (1 - Q_I Q_J) \right. \\
&\qquad \left. + \frac{z'W'_{IJ}}{2kT} c_I c_J (1 + Q_I Q_J)(1 - S_I S_J) \right\}.
\end{aligned} \tag{32}$$

That depends on zW_{IJ}/kT, $z'W'_{IJ}/\mathrm{kT}$ and c_I.

2.3 Thermodynamic quantities of the system

Using the Helmholtz free energy A derived in section 2.1 and 2.2, we can calculate the thermodynamic quantities of the system. Here, we derive the pressure and the entropy explicitly.

The pressure of the system is given by

$$p = -\left(\frac{\partial A}{\partial \mathrm{v}} \right)_T = -\left(\frac{\partial A'}{\partial \mathrm{v}} \right)_T - \left(\frac{\partial A''}{\partial \mathrm{v}} \right)_T = p' + p''. \tag{33}$$

Using Eq. (13), we obtain

$$\frac{p'v}{nkT} = 1 - \frac{1}{kT}\sum_{I,J} c_I c_J \Lambda_{IJ}\left\{p\left(\frac{v_{0IJ}}{v}\right)^2 - q\left(\frac{v_{0IJ}}{v}\right)^4\right\} - \frac{4}{kT}\sum_{I,J} c_I c_J \Lambda_{IJ}\left\{\left(\frac{v_{0IJ}}{v}\right)^2\left(\frac{g_{I,M}}{g_I}\right) - \left(\frac{v_{0IJ}}{v}\right)^4\left(\frac{g_{I,L}}{g_I}\right)\right\} \quad (34)$$

where

$$g_{I,L} = \int_0^{\epsilon} y^{1/2} L(y) \exp\left\{-\sum_{J=1}^{K} \frac{c_J \Lambda_{IJ}}{kT}\left[\left(\frac{v_{0IJ}}{v}\right)^4 L(y) - 2\left(\frac{v_{0IJ}}{v}\right)^2 M(y)\right]\right\} dy \quad (35)$$

and

$$g_{I,M} = \int_0^{\epsilon} y^{1/2} M(y) \exp\left\{-\sum_{J=1}^{K} \frac{c_J \Lambda_{IJ}}{kT}\left[\left(\frac{v_{0IJ}}{v}\right)^4 L(y) - 2\left(\frac{v_{0IJ}}{v}\right)^2 M(y)\right]\right\} dy. \quad (36)$$

To evaluate p'', it is necessary to specify the dependence of W_{IJ} and W'_{IJ} on volume v. Pople and Karasz assumed $W = W_0 (v_0/v)^4$ for their study on plastic crystals. Later, Chandrasekhar *et al.*[9] pointed out that in the case of liquid crystals for which the orientational barriers are large, the assumption of $W = W_0 (v_0/v)^4$ and $W' = W'_0 (v_0/v)^3$ reproduces the experimental results better than the Pople-Karasz's assumption. Therefore, we also assume that $W_{IJ} = W_{0IJ}(v_{0IJ}/v)^4$ and $W'_{IJ} = W'_{0IJ}(v_{0IJ}/v)^3$. Then, from Eq. (32), we obtain

$$\frac{p''v}{nkT} = \sum_{I,J}\left\{\frac{zW_{IJ}}{kT} c_I c_J (1 - Q_I Q_J) + \frac{3}{8}\frac{z'W'_{IJ}}{kT} c_I c_J (1 + Q_I Q_J)(1 - S_I S_J)\right\}. \quad (37)$$

The parameter W_{0IJ} and the parameter ϵ_{0IJ} in Eq. (4) are not independent because they come from the same origin. Bentorf *et al.* determined the ratio $W_0/\epsilon_0 = 0.977$ so as to reproduce the correct melting temperature of argon. Therefore, we also take $W_{0IJ}/\epsilon_{0IJ} = 0.977$.

The entropy of the system is given by

$$S = -\left(\frac{\partial A}{\partial T}\right)_v = -\left(\frac{\partial A'}{\partial T}\right)_v - \left(\frac{\partial A''}{\partial T}\right)_v = S' + S''. \quad (38)$$

Using Eq. (13), we obtain

$$\frac{S'}{nk} = \frac{3}{2}\sum_{I=1}^{K} c_I \ln\left(\frac{2\pi m_I kT}{h^2}\right) + \ln\left(2\pi\frac{\sqrt{2}\,\mathrm{v}}{n}\right) + \sum_{I=1}^{K} c_I \ln g_I + \frac{3}{2} + \frac{1}{kT}\sum_{I=1}^{K} c_I \chi_I \quad (39)$$

where

$$\chi_I = \frac{1}{g_I}\int_0^{\epsilon} y^{1/2}\phi_I(y)\exp\left\{-\frac{\phi_I(y)}{kT}\right\}dy \quad (40)$$

and

$$\phi_I(y) = \sum_{J=1}^{K} c_J \Lambda_{IJ}\left[\left(\frac{v_{0IJ}}{\mathrm{v}}\right)^4 L(y) - 2\left(\frac{v_{0IJ}}{\mathrm{v}}\right)^2 M(y)\right].$$

From Eq. (32), we obtain

$$\frac{S''}{nk} = -\sum_{I=1}^{K} c_I \ln c_I - \left\{\sum_{I=1}^{K}\frac{c_I(1+Q_I)}{2}\right\}\ln\left\{\sum_{I=1}^{K}\frac{c_I(1+Q_I)}{2}\right\} - \left\{\sum_{I=1}^{K}\frac{c_I(1-Q_I)}{2}\right\}\ln\left\{\sum_{I=1}^{K}\frac{c_I(1-Q_I)}{2}\right\} - \sum_{I=1}^{K} c_I\left\{\frac{1+Q_I}{2}\ln\frac{1+Q_I}{2} + \frac{1-Q_I}{2}\ln\frac{1-Q_I}{2} + \frac{1+S_I}{2}\ln\frac{1+S_I}{2} + \frac{1-S_I}{2}\ln\frac{1-S_I}{2}\right\}. \quad (41)$$

The first term of the right hand side of Eq. (41) is the entropy of mixing.

Using Eq. (34) and (37), we can obtain the isotherm of the system, that is, if the interaction parameter ϵ_{0IJ}, W'_{0IJ} and the mole fraction c_I are given, p can be calculated as a function of v with T as a parameter. Actual procedure of numerical calculations are rather complicated and tedious. In the following, we only discuss special examples of binary mixtures of nematogens.

3 PHASE TRANSITION OF BINARY MIXTURES OF NEMATOGENS

In this section, the theory derived in section 2 is applied to the investigation of binary mixtures of A and B components.

First, let us investigate the isotherm of this system. The parameters involved in the calculations of p' are ϵ_{0AA}, ϵ_{0BB}, ϵ_{0AB}, v_{0AA}, v_{0BB}, v_{0AB} and c_A (mole fraction of A component). Therefore, in general case, the calculation is very complicated. So, we restrict the investigation to the case where $\epsilon_{0AA} = \epsilon_{0BB} = \epsilon_{0AB} = \epsilon_0$ and $v_{0AA} = v_{0BB} = v_{0AB} = v_0$. In this case, Eqs. (34), (35) and (36) reduce to those calculated by Bentorf *et al.* Then, we can calculate $p'v_0/nkT$ as a function of (v/v_0) with kT/ϵ_0 as a parameter uniquely.

The parameters involved in the calculation of p'' other than those involved in the calculation of p' are W_{0AA}, W_{0BB}, W_{0AB}, W'_{0AA}, W'_{0BB} and W'_{0AB}. But, as mentioned in section 2.3 ($W_{0IJ}/\epsilon_{0IJ} = 0.977$, we must put $W_{0AA} = W_{0BB} = W_{0AB} = 0.977\epsilon_0$. Therefore, only four parameters W'_{0AA}, W'_{0BB}, W'_{0AB} and c_A are left free to be given. Among them W'_{0AA} and W'_{0BB} are determined by the properties of single-component systems. Therefore, the parameters that are necessary for the investigation of the effect of mixing are only W'_{0AB} and c_A.

Now, let us introduce parameters defined by

$$\begin{cases} \mu_p \equiv W_{0AA}/W_{0BB}, & \nu_p \equiv W_{0AB}/W_{0BB}, \\ \mu_0 \equiv W'_{0AA}/W'_{0BB}, & \nu_0 \equiv W'_{0AB}/W'_{0BB}, \end{cases} \tag{42}$$

$$\kappa \equiv \kappa_B \equiv z'W'_{0BB}/zW_{0BB},\ \kappa_A \equiv z'W'_{0AA}/zW_{0AA} = \kappa\mu_0/\mu_p.$$

The parameters κ_B and κ_A are measures of the relative barriers for the rotation of a molecule and for its diffusion to an interstitial site in pure B-molecule system and pure A-molecule system, respectively. These parameters determine which phases appear in pure A-molecule system or pure B-molecule system. Chandrasekhar *et al.*[9,10] have shown that when κ (in their paper, it is denoted by ν instead of κ) is greater than 0.975, nematic phase appears as an intermediate phase between the solid phase and the isotropic liquid phase.

In the restriction stated above ($W_{0AA} = W_{0BB} = W_{0AB}$), we must put $\mu_p = \nu_p = 1$. The parameters μ_0 and ν_0 are the relative orientational barriers of A-A pairs and A-B pairs with respect to B-B pairs. If we give $\kappa(\equiv\kappa_B)$ and μ_0, κ_A is determined uniquely. Therefore, if we give the values of κ, μ_0, ν_0 and c_A ($\mu_p = \nu_p = 1$), we can calculate an isotherm, i.e., pv_0/nkT as a function of v/v_0 with kT/ϵ_0 as a parameter.

Figure 1 shows an example when $\kappa(\equiv\kappa_B) = 1.15$, $\mu_p = \nu_p = 1$, $\mu_0 = 1.1$, $\nu_0 = \sqrt{\mu_0}$, $c_A = 0.5$ and $kT/\epsilon_0 = 0.66$. In this case, $\kappa_A = 1.265$. So, both of A and B are nematogens. The sigmoid portions in Figure 1 correspond to phase transitions, i.e., the two phases will be in equilibrium at a given pressure and temperature when the areas enclosed by the curve above and below the pressure line are equal (Maxwell's equal-area rule). In Figure 1, C ($v/v_0 = 1.056$, $pv_0/nkT = -0.128$) corresponds to a solid ($Q_A = 0.930$, $Q_B = 0.930$, $S_A = 1.000$, $S_B = 1.000$) and E ($v/v_0 = 1.300$, $pv_0/nkT = -0.128$) corresponds to a nematic phase ($Q_A = Q_B = 0$, $S_A = 0.690$, $S_B = 0.669$). Therefore, C and E

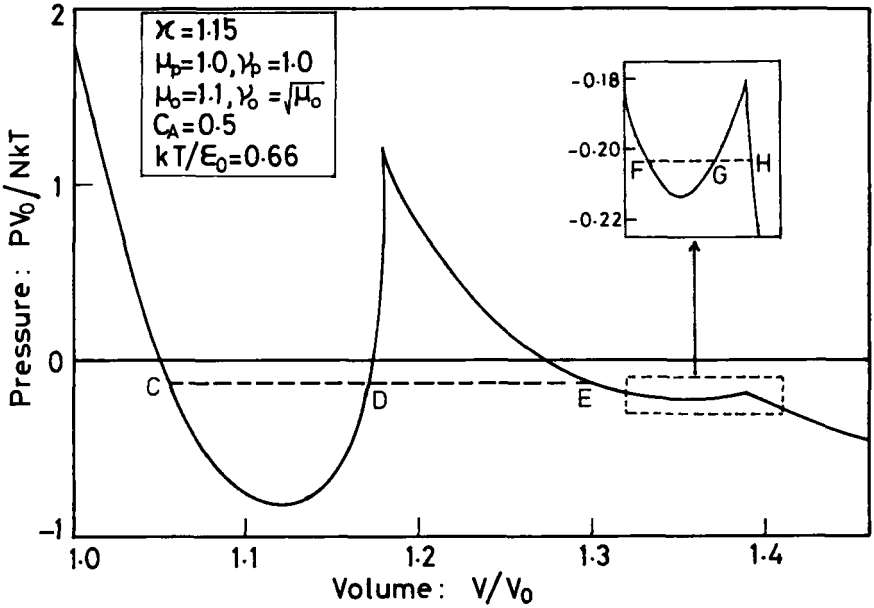

FIGURE 1 Theoretical isotherm of the binary mixture of A- and B-nematogens when $c_A = 0.5$ and $kT/\epsilon_0 = 0.66$.

are in equilibrium at a pressure $pv_0/nkT = -0.128$. Also, we find that a nematic phase F ($v/v_0 = 1.334$, $Q_A = Q_B = 0$, $S_A = 0.567$, $S_B = 0.546$) and an isotropic phase ($v/v_0 = 1.394$, $Q_A = Q_B = S_A = S_B = 0$) are in equilibrium at a pressure $pv_0/nkT = -0.203$.

By changing a temperature, we can obtain the pressure dependence of phase transition temperature. An example is shown in Figure 2 when $\kappa = 1.15$, $\mu_p = \nu_p = 1$, $\mu_0 = 1.1$, $\nu_0 = \sqrt{\mu_0}$ and $c_A = 0.5$. From this figure, we can determine the phase transition temperature at zero pressure. The solid-nematic transition temperature is $kT/\epsilon_0 = 0.6668$ and the nematic-isotropic transition temperature is $kT/\epsilon_0 = 0.6783$. Figure 3 shows the temperature dependence of order parameters at zero pressure. At the solid-nematic transition temperature, Q_A, Q_B, S_A and S_B change discontinuously ($Q_A = 0.928 \rightarrow 0$, $Q_B = 0.928 \rightarrow 0$, $S_A = 1.000 \rightarrow 0.711$, $S_B = 1.000 \rightarrow 0.690$). Also at a nematic-isotropic transition temperature, S_A and S_B change discontinuously ($S_A = 0.482 \rightarrow 0$, $S_B = 0.463 \rightarrow 0$). Both transitions are first order.

By changing the mole fraction of A molecules (c_A), we can construct a phase diagram of the binary mixture of A molecules and B molecules. Figures 4 and 5 show these phase diagrams with ν_0 as a parameter. The parameters κ, μ_p, ν_p and μ_0 are kept constant in these calculations. The phase diagrams are very sensitive to the value of ν_0.

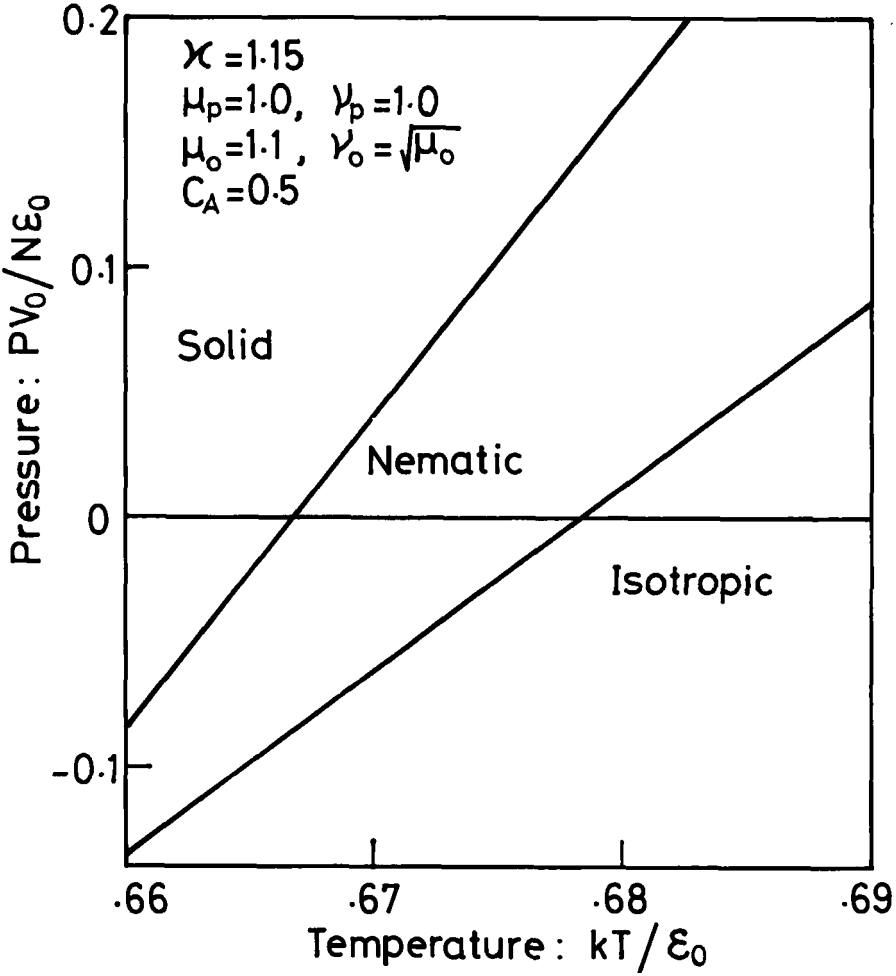

FIGURE 2 Pressure dependence of the phase transition temperatures from the solid solution to the nematic solution and from the nematic solution to the isotropic solution when $c_A = 0.5$.

Figures 6 and 7 show mole fraction dependence of phase transition temperatures from a nematic solution to an isotropic solution, and from a solid solution to a nematic solution, respectively. These are not linear to c_A in general. Only when $\nu_0 = \sqrt{\mu_0}$, the phase transition temperature changes almost linearly to c_A. Strictly speaking, we can show that the transition temperature changes linearly to c_A only when $\nu_p = \sqrt{\mu_p}$, $\nu_0 = \sqrt{\mu_0}$ and $\mu_p = \mu_0$.

The condition $\nu_0 = \sqrt{\mu_0}$ corresponds to $W'_{AB} = (W'_{AA}W'_{BB})^{1/2}$. Therefore, when the orientational interaction energy between an A-molecule and a B-molecule is geometric mean of the orientational energies between A-molecules

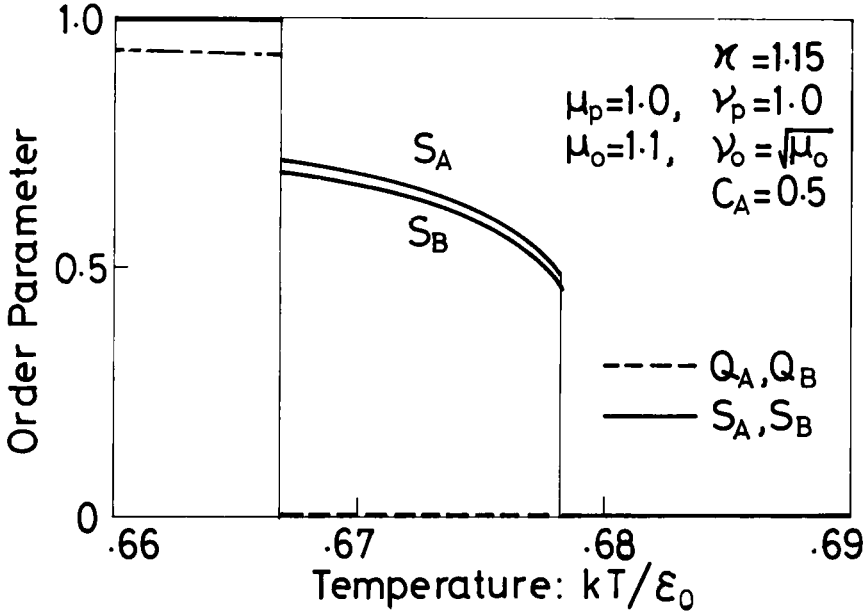

FIGURE 3 Temperature dependence of order parameters at zero pressure when $c_A = 0.5$.

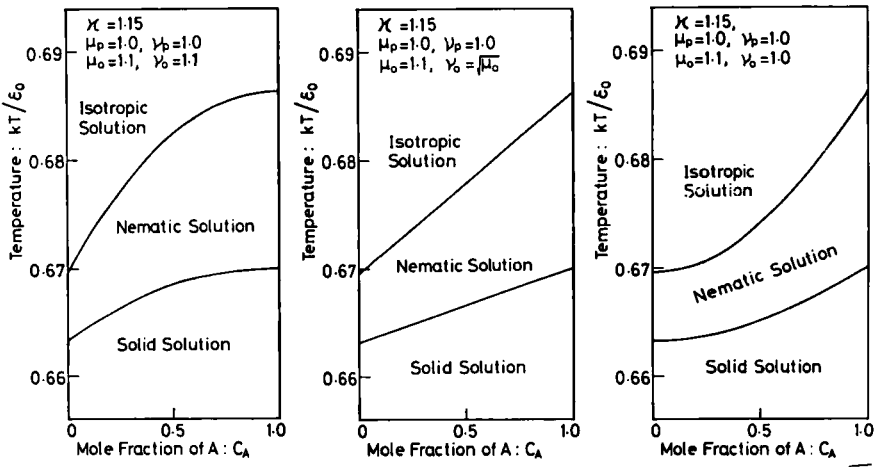

FIGURE 4 Phase diagrams of the binary mixtures of A- and B-nematogens when $\nu_0 = 1.1, \sqrt{\mu_0}$ and 1.0.

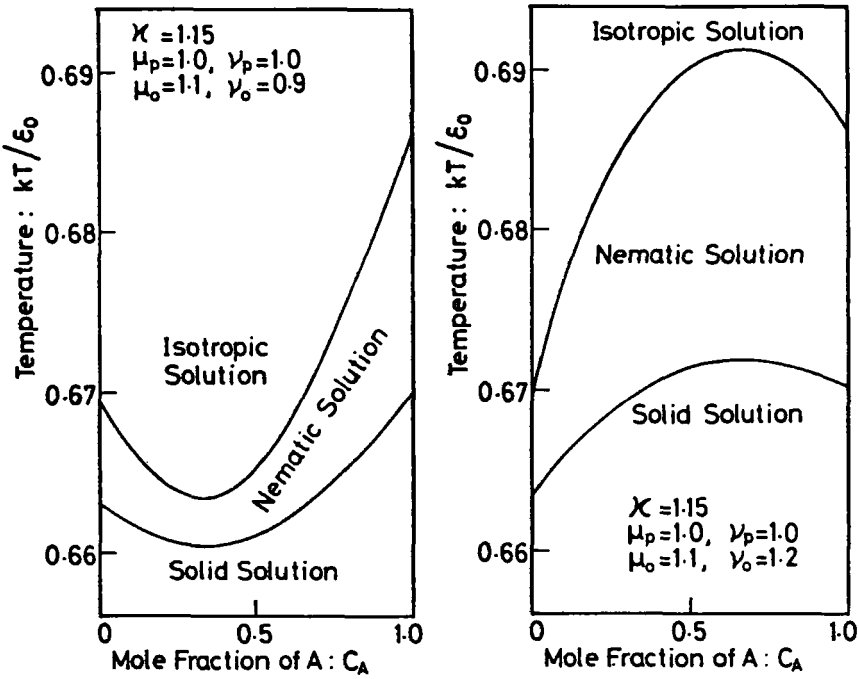

FIGURE 5 Phase diagrams of the binary mixtures of *A*- and *B*-nematogens when $\nu_0 = 0.9$ and 1.2.

and *B*-molecules, the clearing temperature of the binary mixture depends linearly on the mole fraction of *A*-molecules. Humphries *et al.*[1] also derived this result by extending the Maier-Saupe theory to binary mixtures.

In Figure 8, the volume changes at phase transition points are shown. Also these values are affected by the values of ν_0. Using eq. (41), we can calculate the transition entropy. It is shown in Figure 9.

4 DISCUSSION

Numerical calculations given in section 3 implicitly assume that the components of mixtures are mutually soluble at any mole fractions because of the assumption of $\epsilon_{0AA} = \epsilon_{0BB} = \epsilon_{0AB} = \epsilon_0$. It has been known that in the isotropic and nematic phase many binary mixtures of nematogens show this solubility. This perfect solubility, however, is not true in the solid phase. Smith *et al.*[11] observed a solid solution in MBBA-EBBA mixtures. But, it seems that the binary systems of nematogens that constitute a solid solution are rather rare.

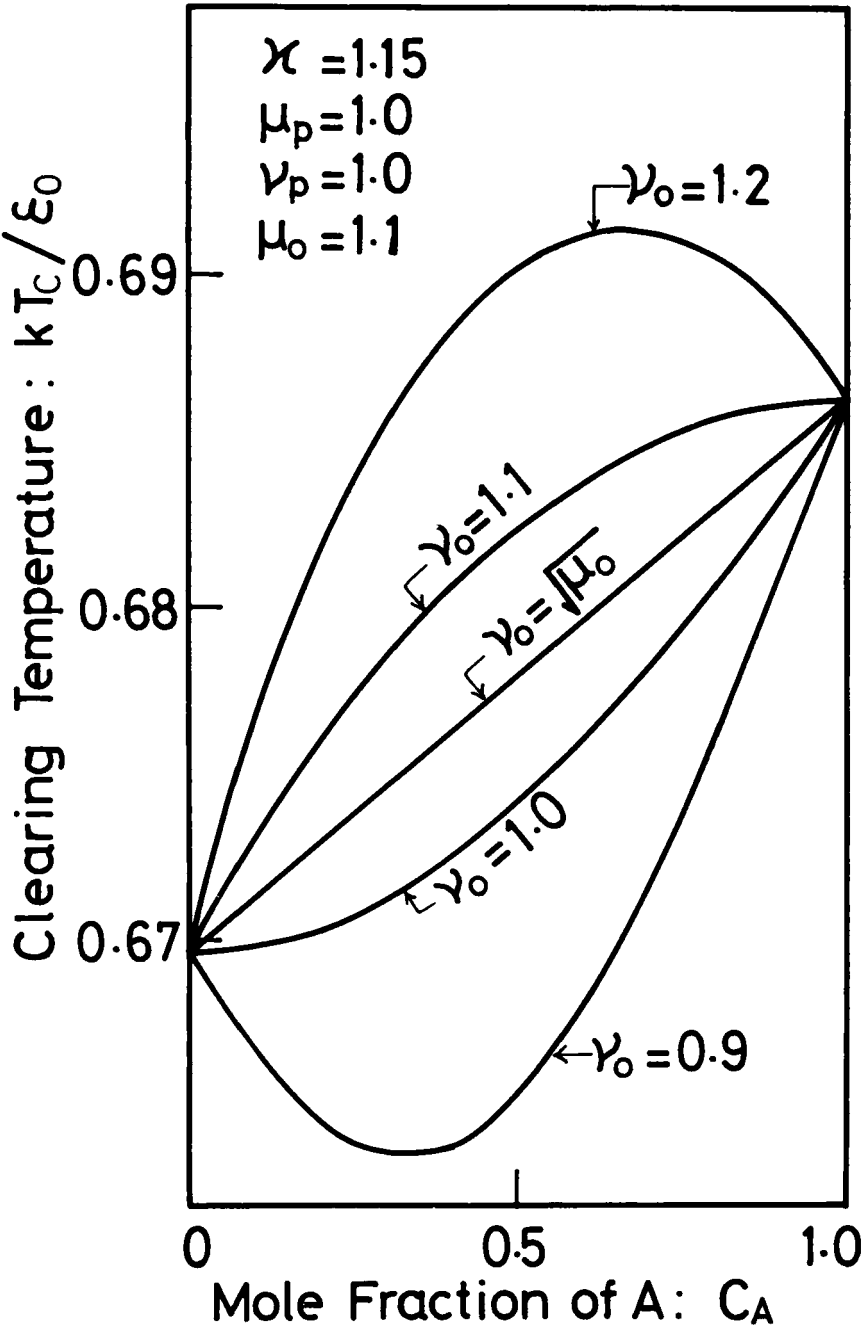

FIGURE 6 Mole fraction dependence of the clearing temperature.

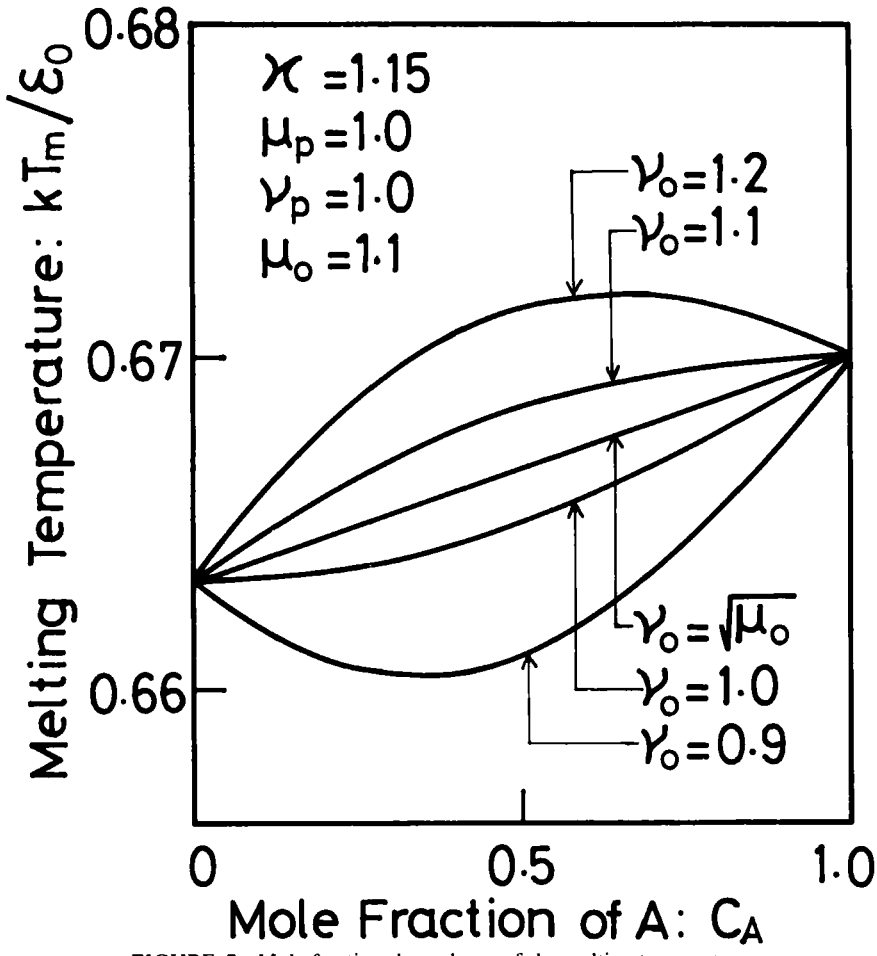

FIGURE 7 Mole fraction dependence of the melting temperature.

To study the solubility problem, we must treat more general cases where ϵ_{0AA}, ϵ_{0BB} and ϵ_{0AB} take different values from each other. In such cases, numerical calculations based on the model stated here become very complicated, but they are still possible. This problem will be studied in near future.

5 CONCLUSION

The Pople-Karasz theory was extended from single- to multi-component mixtures of symmetric, rod-like molecules. A set of equations which determine the

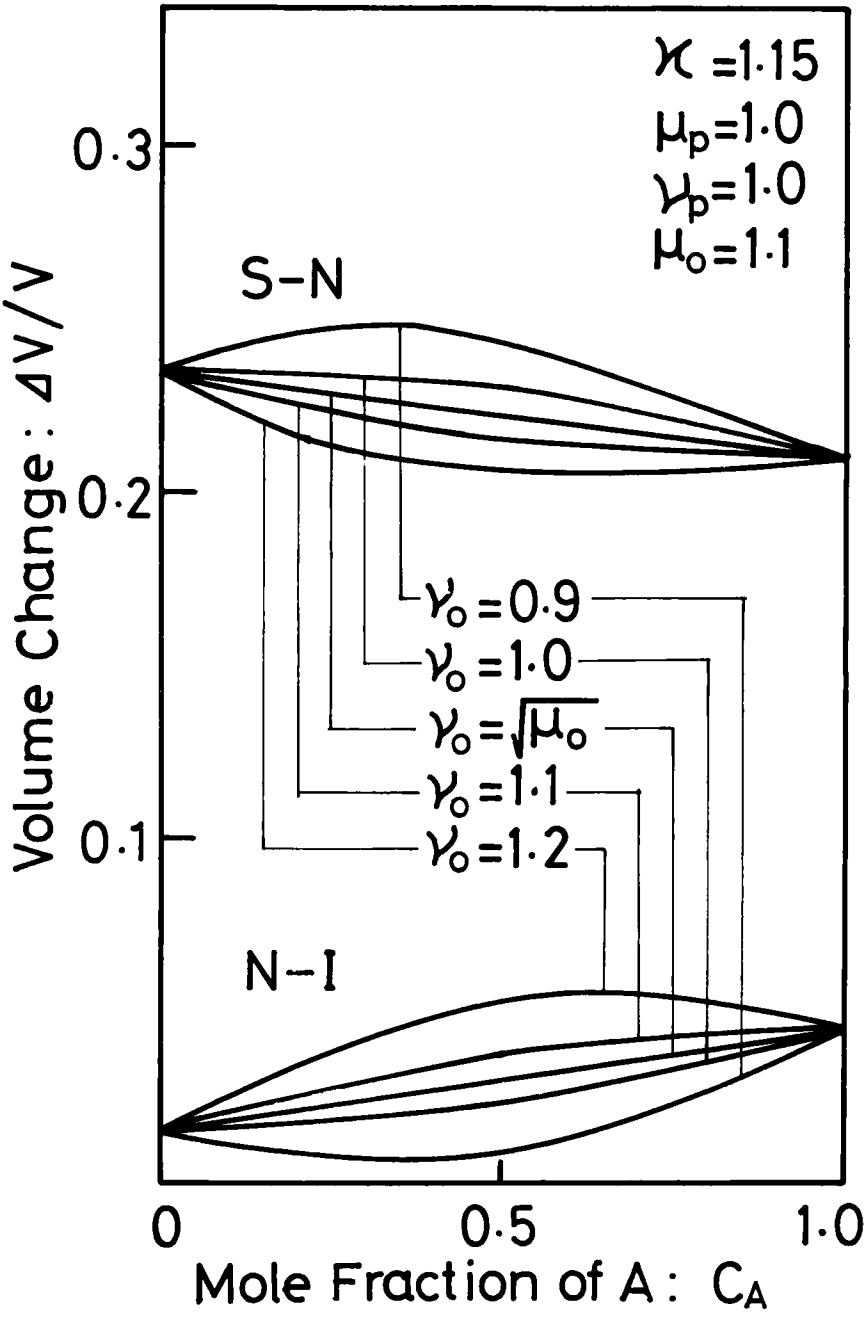

FIGURE 8 Mole fraction dependence of the volume changes at phase transition temperatures.

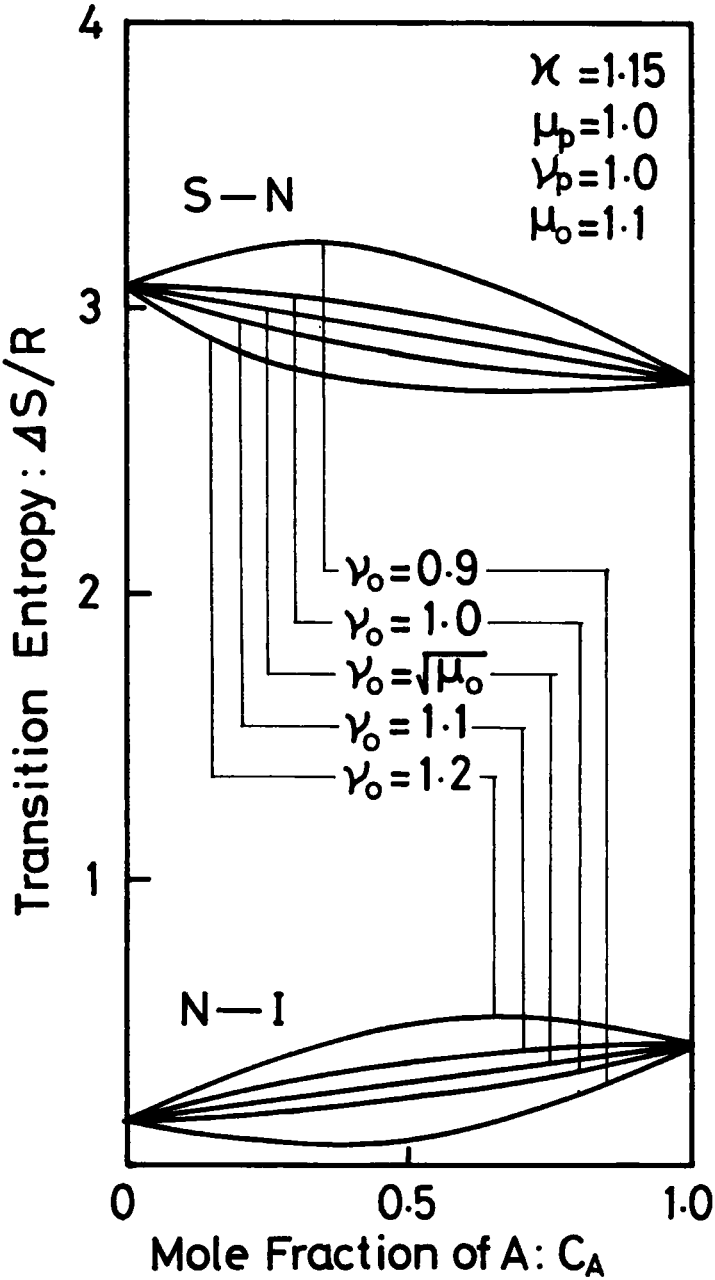

FIGURE 9 Mole fraction dependence of the transition entropies.

orientational and positional order parameters of all components were derived. Thermodynamic quantities such as the pressure and the entropy of the mixtures were obtained.

This theory was applied to investigations of binary mixtures of nematogens. It was shown that the phase diagrams, i.e., mole fraction dependence of phase transition temperatures from the solid solution to the nematic solution and from the nematic solution to the isotropic solution are strongly affected by the interaction energy between molecules of different kinds.

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