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NEMATIC ORDER OF A BINARY SYSTEM : MBBA-BIPHENYL

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Abstract. — A binary system composed of nematogenic solvent (MBBA) and non-nematogenic solute (biphenyl) is investigated for its phase behavior and the dependence of the order parameter on temperature and composition over its entire nematic region. The nematic to isotropic transition temperature is predicted to be a linear function of solute concentration, whereby the dilation effect is shown to be moderated by a measure of orientational anisotropy of the solute molecules, in the context of Maier-Saupe mean field theory. Further, a correspondence relationship between temperature and concentration for the specification of the nematic order parameter is deduced. These predictions are made on the bases of athermal mixing of the two components in the dilute solution limit and of negligible thermal expansion of each component. The experimental phase diagram and justification of athermal mixing from the DSC thermal data are first offered. The order parameter is deduced from the anisotropic optical properties and the correspondence relationship is established by determinations of the order parameter as a function of composition at constant T and of temperature at constant x. Finally, the order surface is constructed from the correspondence relationship.

1. Introduction. — Thermotropic liquid crystals in a single component nematic state have been the subject of intensive studies in the last decade [1, 2, 3]. They can be categorized broadly as addressing two aspects of the system, one dealing with the equilibrium properties of microscopic long range order and the other with the dynamic responses of the order either to spontaneous thermal fluctuations or to a variety of externally imposed force fields. The most successful of the theoretical tools for interpreting the equilibrium properties at the molecular level has been the mean field model of Maier and Saupe [4] in terms of the order parameter; the temperature dependence of order parameter has been formulated in the context of elastic free energy density given by Frank [5] and Oseen [6]. The corresponding theory of the dynamic properties is the linearized hydrodynamic equation of motion by Ericksen [7] and Leslie [8].

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The principal interest in binary systems resides in gaining an additional degree of freedom in thermodynamic characterization of nematic substances. Beyond this, we are interested in extending the analogy between simple liquid crystal systems and biological aggregates which are in most cases complex composite systems such as cell membranes. Phospholipid bilayer membranes of various biological functions and origins are not constituted of one component, but of different phospholipids, proteins, carbohydrates and steroids [9]. Although the liquid crystalline property of these membranes under physiological conditions has been recognized [10] only a limited effort has been expended in delineating the structural changes attended by inclusion or exclusion of minor components except perhaps the effect of cholesterol [11]. A likely possibility is that there exist rather specific interactions in the membrane among the major and minor components. Thus, the necessity for understanding composite systems entails first clearly defining the limiting case where the interactions are non-specific within a binary system. This is the second reason why we have
embarked on a study of the MBBA-biphenyl nematic region.

In this paper, we first outline the theoretical bases of our analysis, then present the results of a macroscopic thermodynamic study in the form of a phase diagram. The non-specificity of interactions in this system will be proven. Next, a study of anisotropic optical properties is presented with the intent of relating them to the nematic order parameter as a function of temperature and composition. We will then show how these two degrees of freedom can be reduced to a single parameter defining the nematic order and a correspondence law between the two can be extracted. The entire analysis is built around the mean field model and the attraction of its simplicity is retained without being encumbered by varying degrees of sophistications [12]. The focus of this report may be stated as follows. Upon addition of a non-nematic component (solute) to a thermotropic nematic (solvent), the order of the entire system is reduced according to a specific rule which is the correspondence principle between temperature and composition, and this relation is entirely predictable from the mean field theory.

2. Preliminary and background. — 2.1 Temperature and Composition Dependence of the Order Parameter. — A brief discussion of the Maier-Saupe model [4] is in order as the starting point. In the mean field theory, the order parameter of uniaxial medium is given by the solution of the following equations in terms of the second order spherical harmonics of the orientational direction [13] that a given molecule, denoted by l, assumes relative to the director of the rest of the system

\[ S_l = \left( \frac{3}{2} \right) \int_0^1 e^{-\frac{d}{2} d^2} \cos^2 \theta_l \, d(cos \theta) \int_0^1 e^{-\frac{d}{2} d^2} \cos \theta_l \, d(cos \theta) - \frac{1}{2} \]  

(1)

with

\[ D = - \left( A/2 \bar{V}^2 \right) S(3 \cos^2 \theta_l - 1) \]  

(2)

under the self-consistent condition of equilibrium for the nematic system,

\[ S_1 = S \quad \text{and} \quad dS/dS < 1 . \]  

(3)

Here, \( \theta_l \) is the angle between the lth major molecular axis and the director. The definitions of notation may be summarized in combination with the assumptions invoked for the above equations as follows:

1) The intermolecular interaction energy ensuring the nematic state is solely due to the dispersion terms (the second order perturbation) of the intermolecular forces. Electrostatic interactions, induction forces, as well as other perturbation interactions (multipole-multipole), etc. [14], are all assumed to be of negligible importance in establishing nematic order.

2) The short range repulsive interactions are somewhat artificially taken into account by arguing that these drive the system to form microscopic aggregates of few molecules each (the exact number being unspecified) within which the alignment of constituent molecules is absolutely uniform. Hence, the meaning of \( \theta_l \) in eq. (1) and (2) is modified to refer to these aggregates.

3) All molecules (strictly, the aggregates referred to above) in a nematic phase are in their ground electronic states, and to the anisotropic part of the transition moments from the ground state is ascribed the predominant contribution to the dispersion energy.

4) The distribution of the centers of mass of molecules (aggregates) is spherically symmetric within a macroscopic volume.

Thus, the meaning of \( A \) in eq. (2) may be understood as the ratio of the averaged sum of the orientation dependent oscillator strengths to the corresponding transition energy from the ground state to the electronically excited states of a molecule; hence, \( A \) is a characteristic material constant. The dependence of the dispersion energy on the spherically symmetric distribution of intermolecular separations introduces a \( V^2 \) term in the denominator of eq. (2) where it stands for the square of the molar volume. One of our tools in studying a binary system is through this \( R^{-6} \) dependence of the theory.

The solution of eq. (1) and (3) provides the following bounds:

A) The order parameter \( S \) at the nematic to isotropic transition is roughly a universal constant of 0.44 independent of the nematic substance.

B) The quantity of \( A/kT_e \bar{V}_e^2 \) has nearly the same value of 4.55 at the transition point with the temperature \( T_e \) and the molar volume \( \bar{V}_e \).

C) Hence, the degree of order \( S \) is a unique function of \( T \bar{V}^2/T_e \bar{V}_e^2 \) within the nematic region for all such systems.

We now examine how \( S \) is affected by dilation of the spacial distribution of these molecules upon addition of a passive second component whose effect is merely to expand the distance among the interacting nematogenic molecules. Assume that there is no volume of mixing when the second component with mole fraction \( X \) is added to a pure nematic substance. Then,

\[ \bar{V}_e(T_e, X) = \bar{V}_e^0(T_e) + \left( \frac{X}{1-X} \right) \bar{V}_e^0(T_e) \]

\[ = \bar{V}_e^0(T_e) \left[ 1 + \left( \frac{X}{1-X} \right) \phi(T_e) \right] \]  

(4)

with \( \phi(T_e) \equiv \bar{V}_e^0/\bar{V}_e^0 < 1 \) for the cases considered, where \( \bar{V}_e(T_e, X) \) is the volume of mixture required to contain one mole of solvent at the nematic to isotropic transition of the mixture, and \( \bar{V}_e^0(T_e) \) are
the molar volumes of the solvent and solute (non-
nematic by itself) at their respective pure states
at $T_\alpha$. If the thermal expansion coefficients of each
component are assumed to be small [15] within the
nematic phase region of the solution then

$$T_c(X) = A/4.55 \kappa^2 \varphi^2(X)$$

$$= [A/4.55 \kappa^2 \varphi^2(T_c)] \left( 1 + \frac{X}{1 - X} \right)$$

$$\times \left\{ 1 - 2 \varphi X + (3 \varphi - 2) \varphi X^2 + \cdots \right\}$$

provided $X < 0.5$. In the dilute solution, we then
expect that

$$T_c(X) = T_c(0) (1 - 2 \varphi X)$$

(6)

where $T_c(0)$ is the transition temperature of pure
solvent component. This simple result predicts that
the transition temperature of a binary nematic system
is a linear function of the concentration of
non-nematic solute in the dilute solution limit and its
relative change from that of pure thermotropic one
deals on the ratio of molar volumes of the two
components. An implicit assumption here is that the
molecular orientation of the solute component is
spherically symmetric in the solution; this should be
reasonable for spherical solute molecules such as
carbon tetrachloride or methane but is less plausible
for non-spherical molecules if their orientational
distribution function in nematic solution deviates
from the spherical symmetry. In such a case, the
dilation effect by the solute would be less than that
deduced using the spherical factor $2 \varphi T_c(0)$ and the
relative deviation could in turn be used as a measure
of the orientational order of the solute component [16].

Returning to the third prediction of the Maier-
Saupe theory that the order parameter $S$ is a unique
function of $TV^2(T)/T_\alpha V^2(T_c)$ for pure thermotropic
systems, a parallel conclusion can be drawn for
binary solutions of the kind with which we are con-
cerned. If the solute were to pack normal to the align-
ment direction, it would sample the volume fraction.
The density accounting by mole fraction is valid
only when uniform alignment of nematic system is
assumed and the alignment is not substantially per-
turbed by the introduction of solute. It should be
noted here that the volume of solution necessary to
contain one mole of solvent in eq. (4) is formulated
without the uniform alignment constraint, hence the
accounting procedure is different from $N(T, X)$. A
further difference between $V_c(T, X)$ and $N(T, X)$ is
that the former refers to the isotropic intermolecular
distance of interacting moieties while the latter refers

and Madhusudana [17] by assuming the internal
polarization field to be of the Lorentz-Lorenz type
as Vuk's [18] has done with organic molecular crystals.
The following expressions are given:

$$\frac{n_s^2 - 1}{n_s^2 + 2} = \frac{4 \pi N}{3} \left( \Delta x + \frac{2}{3} \Delta S \right)$$

(8)

$$\frac{n_0^2 - 1}{n_0^2 + 2} = \frac{4 \pi N}{3} \left( \Delta x - \frac{1}{3} \Delta S \right)$$

(9)

or alternatively

$$\frac{n_s^2 - n_0^2}{n_s^2 + 2} = \frac{4 \pi N}{3} (\Delta \alpha) S$$

(10)

where $n_s$ and $n_0$ are the extraordinary and the ordinary
refractive indices respectively, the mean refractive
index $n^2 = \frac{1}{2}(n_s^2 + 2 n_0^2)$, the mean polarizability of
a nematogenic molecule $\bar{\alpha} = \frac{1}{2}(\alpha_s + 2 \alpha_0)$, the
anisotropy of molecular polarizability $\Delta \alpha = (\alpha_s - \alpha_0)$,
and $N$ is the number density of the nematogenic
molecule. Assuming that the solute component does
not contribute to the birefringence of the solution
while it does to the order parameter through the
$V^2(T)$ term, the modification of eq. (10) for binary
systems is accomplished by expressing the number
density $N$ as

$$N(T, X) = N^0(T) (1 - X)$$

(11)

where $N^0(T)$ is the number density in a pure thermo-
tropic system. The basis for expressing the number
density of the solvent molecules by its mole fraction
comes from the consideration of the nematic packing
problem of Flory [19] and DiMarzio [20]. It may
be briefly stated as follows. Consider a system consist-
ing of cylinders of a given diameter with equal
length which are uniformly aligned in a lattice. In
the athermal limit [21] ($\Delta H_0 = 0, \Delta V_0 = 0, \Delta S_m \neq 0$),
the introduction of a second component which has
the same diameter but a different length into the lattice,
produces a density decrease of the first component
which is accounted for by the number fraction (or
mole fraction) because each solute molecule samples
the cylinder's cross sectional area (normal to the
cylindrical axis) and this is the same for both compo-
nents. If the solute were to pack normal to the align-
ment direction, it would sample the volume fraction.

The density accounting by mole fraction is valid
in the dilute limit. In the above equation, a positive
constant $\sigma \ll 1$ is introduced as a measure of the
degree of anisotropy in the orientational distribution
of the intercalated solute molecules.

2.2 Order parameter determination. — The opti-
cal technique for the determination of the order
parameter has been formulated by Chandrasekhar
to the macroscopic number density of optically anisotropic molecules.

Substitution of eq. (11) into eq. (10) yields the order parameter,

\[ S = \frac{3}{4\pi} \left( \frac{n_{\infty}^2 - n_0^2}{n^2 + 2} \right) \left[ N^0(T)(1 - X) \Delta \alpha \right]^{-1}. \]  

(12)

Through this equation the order parameter as a function of \( T \) and \( X \) can now be tested for its unique functional dependence with respect to the single variable of reduced temperature \( \tau(T, X) \).

In closing this section, we summarize the necessary background for the interpretation of our findings which will follow. If the binary system under consideration is accessible by visual observation could be determined by the DSC method. The temperature scale as well as the endothermic peak area for a DuPont Thermal Analyzer [23] (Model 900) were calibrated with five samples of gallium \( (T_m = 29.78{^\circ}C, \Delta h_f = 19.1 \text{cal/g}) \). Each sample was hermetically sealed in an aluminum planchet, preheated to the isotropic liquid state, then quenched in liquid nitrogen. The heating rates were programmed at 3.5 \( ^\circ\text{C/min} \) and 7.0 \( ^\circ\text{C/min} \). The accuracy in the heating rate was within 5 \( \% \) and the linearity with respect to time within 1 \( \% \). The two heating rates produced no difference in the results.

3.3 Optical properties. — The technique of birefringence measurement on an aligned nematic system was that of Haller et al. [24] with minor refinements. The cell was made by cutting in half a single microscopic slide glass which had been previously treated for alignment and forming into a wedge. The wedge angle was measured by mounting the cell with the apex at the center of a goniometer (Bridgeport rotary table, RT-15) and reflecting a laser beam from the two surfaces, so that the circular reflection from each plate was successively centered around a wire 15 feet away from the apex. The uncertainty in the wedge angle was determined as 0.3 \( \% \). The fringe spacing as observed by a polarizing microscope (90 X) with travelling stage, the wedge angle, and the wave length of the He-Ne laser light source are combined to determine the birefringence through a simple optical phase relationship. An uncertainty of 0.5 \( \% \) was assigned for the birefringence values for the isothermal run \( (23{^\circ}C) \) for the concentration range of 0-8.35 mole \% biphenyl, and 1.5 \( \% \) uncertainty for the constant composition run \( (8.13 \text{ mole } \% \text{ biphenyl}) \) over the temperature range 16-26 \( ^\circ\text{C} \). Temperature was controlled by room thermostat and monitored by a thermometer and a thermocouple placed at the wedge surface.

The ordinary refractive index was measured by an Abbe refractometer (Carl Zeiss) with a diffuse He-Ne laser source. The refractometer was calibrated with doubly distilled benzene as the standard, using the value of \( n_{6328,20^\circ\text{C}} \) (benzene) = 1.4975 and

\[ \frac{dn}{dT} = 6.4 \times 10^{-4}/^\circ\text{C}. \]

(Uncertainty in \( n_0 \) values was assigned as \( \pm 0.001 \).

4. Results and discussion. — 4.1 Phase diagram. — As shown in figure 1, the phase diagram obtained by visual observation and the DSC method provides...
NEMATIC ORDER OF A BINARY SYSTEM: MBBA-BIPHENYL

FIG. 1. - A portion of the Phase Diagram of MBBA/biphenyl. Filled circles refer to the results of visual observation and rectangles to those of the DSC measurement.

Area A: Solid MBBA + Isotropic Solution
B: Solid MBBA + nematic liquid crystal
C: Nematic liquid crystal
D: Nematic liquid crystal + isotropic solution
E: Isotropic Solution.

a coherent picture of phase transformations. The existence of a biphasic region between the nematic state and the isotropic solution is unmistakable. Although one observes a variety of metastable phases by the DSC method [25] (below the temperature scale in figure 1), we represent only a part of the entire phase diagram to restrict ourselves to the relevant features of this paper. An additional observation was noted in the biphasic region; when the fraction of either the nematic phase or the isotropic phase is dominant, i.e., in the vicinity of the coexistence curves, the whole system appeared as a single phase, either nematic or isotropic, for a period of time (5-30 min) following vigorous shaking before the phase boundary reappeared when allowed to stand. We attribute this phenomenon as the probable cause of the controversy [26] surrounding the existence of a biphasic region which is completely consistent with the first order phase transition [27]. Stability of a biphasic region was tested by letting one sample stand at ambient temperature for a period of over one-half year. No change was detected in the relative proportion of each phase.

The biphasic transition region precludes the observation of the temperature $T_c(X)$ at which isotropic and nematic liquids of composition $X$ are in equilibrium. The first appearance of isotropic liquid in a multicomponent system occurs at phase separation which will be at a temperature slightly lower than that at which the anisotropic free energy disappears ($T_c$). Bearing in mind that this is a small effect [25] we may consider $T_c$ to be satisfactorily approximated by the temperature at which the nematic is unstable with respect to phase separation.

The initial portion of the phase diagram confirms qualitatively the prediction of eq. (6) or (6'), meaning that the $R^{-6}$ dependence of the dispersion energy in the mean field theory is consistent with our observation. Detailed analyses are rendered as follows. The molar volume ratio $\varphi$ of biphenyl to MBBA is calculated from the densities of the two components, biphenyl in liquid state [28] at 70 $^\circ$C and MBBA in nematic state at 25 $^\circ$C. The calculated $\delta T_c(X)/\delta X$ is larger than the observed one by 40%. The discrepancy is expected as pointed out in Section 2 because of the alignment of the solute in the nematic solution. On this basis alone it would be insufficient to confirm or refute the hypothesis put forth in Section 2. We can, however, seek other supportive evidence; the composition dependence of the transition temperature has been investigated with several solute-solvent pairs by Peterson and Martire [29] as well as Hillenbrand [30] in this laboratory. These are collected in Table I, which demonstrate the validity of the hypothesis in as much as spherical or small solute molecules produce a full effect of dilution, i.e., $\sigma = 1$, whereas

### Table I

Comparison of the observed and the calculated linear terms of the composition dependence of the nematic-isotropic transition temperature in binary systems

<table>
<thead>
<tr>
<th>System</th>
<th>Observed $(\delta T_c(X)/\delta X)$ ($^\circ$C/mole fraction)</th>
<th>Molar volume ratio $\varphi$</th>
<th>Calculated $(\delta T_c(X)/\delta X)$ ($^\circ$C/mole fraction)</th>
<th>$\sigma$ ($^\circ$C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MBBA/Biphenyl</td>
<td>- 250</td>
<td>0.63</td>
<td>- 402</td>
<td>0.62</td>
</tr>
<tr>
<td>MBPA/n-Heptane (1)</td>
<td>- 222</td>
<td>0.58</td>
<td>- 386</td>
<td>0.58</td>
</tr>
<tr>
<td>HAB/MFB (2)</td>
<td>- 156</td>
<td>0.24</td>
<td>- 190</td>
<td>0.82</td>
</tr>
<tr>
<td>MBPA/Benzene (3)</td>
<td>- 222</td>
<td>0.35</td>
<td>- 234</td>
<td>0.95</td>
</tr>
<tr>
<td>MBPA/CCl4 (4)</td>
<td>- 236</td>
<td>0.38</td>
<td>- 254</td>
<td>0.93</td>
</tr>
</tbody>
</table>

(1) Calculated according to eq. (6).
(2) Calculated through eq. (6').
(3) p-methoxybenzylidene-p'-propylaniline; reference [29].
(4) p,p'-hexyloxyazoxybenzene in monofluorobenzene; reference [30].
asymmetric solutes either rigid or flexible, give rise to an attenuated effect. In fact, one can integrate the magnetic resonance studies of asymmetric solute dissolved in nematogenic solvent with thermodynamic analysis so as to quantify the anisotropic factor at the molecular level [31]. In any event, the phase study seems to lend support to the $R^{-n}$ dependence of the mean field theory under the assumption that there exists no specific interaction between the two components.

We will now present the experimental result to justify the athermal assumption. From the DSC method we obtain the specific latent heat by graphical integration of the thermograms at two transitions, crystal to nematic and nematic to isotropic. The results are displayed in figure 2 where the total specific latent heat is plotted against mole fraction of biphenyl. With the athermal assumption for the binary system, the expression for the total specific latent heat [32] is

$$
\Delta h = \Delta h_1^0 + \frac{M_2}{M_1} (\Delta h_2^0 - \Delta h_2) X + \cdots \text{(cal/g)} \tag{13}
$$

where $\Delta h_1^0$ and $\Delta h_2^0$ are the specific latent heats of pure solvent and solute respectively, and $M_1$ and $M_2$ are the corresponding molecular weights. Thus, eq. (13) provides a means to interpret the result of figure 2 in the dilute solution limit. It can be accomplished if $\Delta h_1^0$ and $\Delta h_2^0$ are known from other measurements or a linear approximation of the data in figure 2 yields a sensible set of the values. We choose to proceed along the former route. The value of $\Delta h_1^0$ is estimated as follows. From the coexistence line of the solid and nematic phases in the phase diagram, one determines the molar latent heat of pure MBBA at the solid-nematic transition with the aid of van’t Hoff’s law; the result is

$$
\Delta H_{KN} = 3.70 \pm 0.15 \text{ kcal/mole}.
$$

From the DSC thermogram, the same quantity at the nematic-isotropic transition is deduced as $76 \pm 1 \text{ cal/mole}$ which is in good accord with the values of $75 \text{ cal/mole}$ [33] and $79 \text{ cal/mole}$ [34] reported in the literature. We therefore estimate

$$
\Delta h_2^0 = 14.2 \text{ cal/g}
$$

for MBBA. From the thermodynamic table, we find $\Delta h_2^0 = 30.4 \text{ cal/g}$ for biphenyl [35]. Thus the composition dependence of the total specific latent heat is to be tested against eq. (13). Upon substituting these values into the equation, we obtain the solid line drawn in figure 2, indicating a fair agreement with the experimental data. Hence, the assumption of non-specific interaction is borne out by the experiment.

4.2 ORDER PARAMETER. — The birefringence results of two perpendicular scans within the nematic region of the phase diagram are displayed in figure 3. The first one is along the isotherm at $23^\circ C$ at different concentrations and the other is along the isopleth of composition at $X = 0.081$ at different temperatures. For the case of the composition scan, a combination
of the birefringence with the ordinary refractive index measurement yields a full determination of \( n_o \) and \( n_e \), and these are displayed in figure 4. The purpose here is to demonstrate that the order parameter determined through eq. (12) is uniquely characterized by the reduced temperature \( \tau(T, X) \). A major consequence of such a characterization is that one is able to map out the order parameter over the entire nematic region by performing only a limited number of scans with respect to \( T \) and \( X \).

The hypothesis is verified in the following manner. We first plot \([S \Delta \alpha N^0(T)]\) against \( \tau(T, X) \) for pure MBBA and then for the isothermal data at 23°C, and compare the two. For the case of pure MBBA, we use the data of Haller et al. [24] against \( \tau(T, 0) \) and in the second the data in figure 4 are plotted against \( \tau(296 \text{ K}, X) \) where the expression for \( \tau(T, X) \) is as in eq. (7). The results are shown in figure 5 and the agreement between the two is excellent. The main reason for presenting the data by means of \([S \Delta \alpha N^0(T)]\) instead of \( S \) is to avoid introducing \( \Delta \alpha \) as an adjustable parameter in the absence of any available experimental data, which may appear to weaken the case. Despite our inability to deduce the absolute value of \( S \), the predicted correspondence between \( T \) and \( X \) with respect to the order parameter is apparent from figure 5. It should also be noted that \( \tau(T, X) \) for the composition scan is calculated through eq. (6') and (7) with the values of \( T_o(0) = 319 \text{ K} \) and \( \sigma = 0.6 \). Complementary evidence of the validity of \( T-X \) scaling is offered as follows. Instead of the CMV scheme of inferring the nematic order from the optical properties, a further approximation is effected by neglecting the internal polarization field as in Chatelain's original proposal [36] to let \( S \) be proportional to the observed birefringence. Since we do not have on hand the values of ordinary refractive index as a function of temperature at \( X = 0.081 \), we resort to the Chatelain approximation in order to extract \( S \) [for the data in Fig. 3(8)]. Thus, we plot \( \Delta n/(1 - X) \) against \( \tau(T, 0.081) \) and compare it to that obtained for pure MBBA [24]. With use of \( T_o(0) = 319 \text{ K} \) and \( \sigma = 0.6 \) as before, the results are as shown in figure 6 which demonstrates an excellent agreement. This comparison has been between two parallel temperature scans separated by a constant composition of 8.1 mole % of biphenyl whereas the previous one was between two perpendicular scans in \( T-X \) plane of the phase diagram.

These two pieces of evidence offered above make it obvious that a correspondence principle of \( T \) and \( X \) is well established for the MBBA/biphenyl system. Whether such a scaling principle is of general applicability to any athermal mixture remains to be tested. The molecular basis for the correspondence, as outlined in Section 2, is seen to be consistent with the mean field model of Maier and Saupe. Thus equipped with the \( T-X \) scaling, we now proceed to map out the \( S \)-surface relative to \( T \) and \( X \) via eq. (6') and (7). An \( S \)-surface so constructed is shown in figure 7. The significance of such a surface is to provide a
set of equi-order lines projected on T-X plane which are approximately parallel to the coexistence line of nematic-isotropic transition. One should note that they are not strictly parallel to the coexistence line because there is an evidence for further reduction in S of the anisotropic phase in equilibrium with isotropic phase as we have observed by the NMR linewidth study [30]. The detail of such a study will be the subject of future publications.

Acknowledgments. — We wish to acknowledge the support of the Biomedical Sciences Program of NIH administered by the Graduate School of the University of Wisconsin and of a NIH grant, GB-15432.

References

[15] Noting that the thermal expansion coefficients of chemicals in questions are of the order of 10^{-3}°C and the temperature range of nematic region of about 20°C, this assumption amounts to neglecting a few percent in volume change which is consistent with the degree of approximation adopted throughout the paper.
[23] We gratefully acknowledge Professor S. L. Cooper for the loan of instrument and Dr. J. West for his assistance.
[31] HILDENBRAND, D. F. and YU, H., to be published.
[32] Although we have assumed σ to be independent of T and X as a first approximation, there exists ample evidence to indicate otherwise in the literature. See for example, SVEDEBERG, T., Kolloid Z. 16 (1915) 103; SAUPE, A., Acta Crystallogr. 1 (1966) 527; DREHL, F. and KHETRAPAL, C. L., Mol. Phys. 14 (1967) 283.
[34] Under the assumption of athermal mixing in both the nematic and isotropic liquid phases, we ignore the

![Fig. 7. — Nematic order surface of MBBA/Biphenyl system. S-axis is in an arbitrary unit.](image-url)
enthalpy of mixing in both, and further assume that the enthalpy of transition of non-nematogenic component is that of solid-liquid equilibrium. Total specific enthalpy of transition for a binary liquid is then given by

$$\Delta h = (1 - \omega_2) \Delta h_1^0 + \omega_2 \Delta h_2^0$$

where $\omega_2$ is the weight fraction of solute component which can be written as

$$\omega_2 = n_2 M_2 / (n_1 M_1 + n_2 M_2) =
\frac{X M_2}{(1 - X) M_1} \left[ 1 + \frac{X M_2}{(1 - X) M_1} \right]^{-1} - \frac{M_2}{M_1} X + O \left( \frac{M_2}{M_1} X^2 \right)$$

with $X = n_2 / (n_1 + n_2)$.

Retaining only the term linear in $X$ in the weight fraction, we can express

$$\Delta h = \Delta h_1^0 + \frac{M_2}{M_1} (\Delta h_2^0 - \Delta h_1^0) X + \ldots$$

which is eq. (13).