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On the Phase Transition Behaviour of Binary Systems:

Various Non-Nematic Solutes in Nematic Solvent (EBBA)

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Phase transition behaviour of the systems of EBBA with methyl alcohol (MeOH), 1,2-dibromoethylene (DBE), *o*-xylene, *m*-xylene, and *p*-xylene has been studied. The phase diagrams for each system have been determined by the polarizing microscope. The slopes, β_n and β_i , of the nematic and the isotropic phase boundary lines in each system have been qualitatively described by the molecular field treatment proposed by Humphries. The order parameters for both *cis*- and *trans*-DBE in EBBA have been obtained from analyses of ^1H -NMR spectra. In the nematic phase, they decrease with increase in temperature. In the nematic/isotropic coexisting phase (N/I phase), the order parameter for *cis*-DBE is almost independent of temperature. The proton spin-lattice relaxation times (T_1) in the MeOH/EBBA system have been measured by a pulse NMR technique. Little temperature dependence of T_1 has been found in the N/I phase region.

INTRODUCTION

It is well known that non-mesomorphic solutes depress the isotropic to nematic transition temperature in liquid crystals. Humphries, James and Luckhurst^{1,2} (HJL) have extended the Maier-Saupe³ theory of the nematic mesophase to multicomponent systems. The qualitative conclusions predicted by their theory were in accord with experimental results reported by Martire⁴ *et al* using gas chromatography and microbalance for the boundary region in nematic-isotropic coexisting phase (N/I phase).

^1H -NMR is a useful technique to study the degree of orientation and the structure of liquid crystals, and the complete phase diagram for binary mixture systems has been extensively studied by this method.^{5–14} Little experimental data, however, have been reported concerning temperature and concentration dependence of the order parameter in N/I phase.

Proton spin-lattice relaxation has been also studied on liquid crystals by many investigators.¹⁵⁻¹⁹ Previous studies have shown that the intramolecular dipolar interaction between a proton pair caused by the long-range order fluctuations and the short-range molecular reorientations is a dominant factor in the spin-lattice relaxation in the nematic phase.

We focus our attention on the isotropic-nematic phase transition. Temperature dependence of the phase boundary lines will be discussed by considering the formulae derived by HJL. Also, the results of the measurements of the order parameter for partially oriented molecules in the liquid crystal and the proton T_1 of the mixture system are given.

EXPERIMENTAL

The liquid crystal, N-(*p*-ethoxybenzylidene)-*p*-butylaniline (EBBA), was obtained from Eastman Kodak and used without further purification. The clearing point temperature and the solid to nematic phase transition temperature are reported to be 80°C and 37°C, respectively.²⁰ Methyl alcohol, 1,2-dibromomethylene, *o*-xylene (*o*-X), *m*-xylene (*m*-X), and *p*-xylene (*p*-X) were commercially available. A mixture of *cis* and *trans* forms of 1,2-dibromoethylene was used. The ratio of *cis*- and *trans*-DBE was found to be 60:40 by gas chromatography through measured temperature range.

The observation by a polarizing microscope (P.M.) was made with a Nikon P.M. POH. The sample temperature was measured by a thermocouple detector.

The ¹H-NMR spectra were recorded at 100 MHz with a JEOL JNM-PS 100 spectrometer equipped with JEOL variable temperature assembly. The probe temperature was measured with a thermocouple detector. The samples were not rotated around the vertical axes.

The proton spin-lattice relaxation times were measured at 60 MHz using a JEOL pulse NMR-JSE 5 spectrometer. The width of 90° pulse was about 2 μsec, and the receiver deadtime was about 10 μsec. The data were obtained using repeated 90°-τ-90° pulse sequences.

RESULTS AND DISCUSSION

1 Phase diagram

The phase diagram of a binary mixture, non-nematic solute in nematic solvent, is characterized by the appearance of an intermediate coexisting phase. A typical phase diagram for such a system is shown in Figure 1.

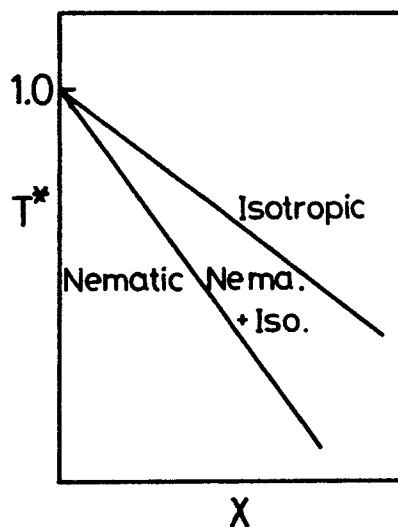


FIGURE 1 Typical diagram of reduced temperature (T^*) vs. mole fraction of solute (X).

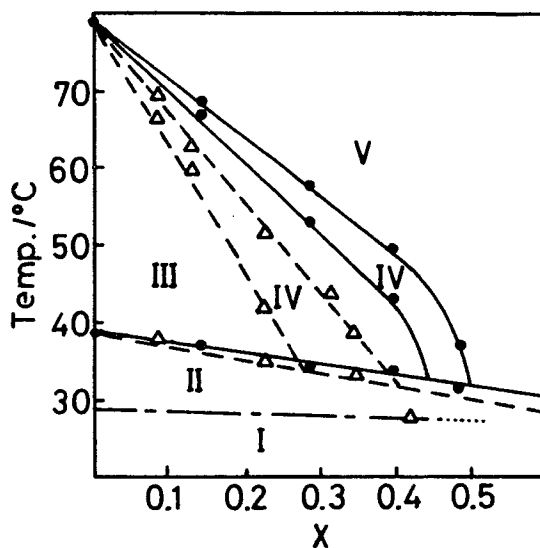


FIGURE 2 Phase diagrams determined by the polarizing microscope. ● MeOH/EBBA; △ DBE/EBBA I S/I phase; II S/N phase; III N phase; IV N/I phase; V I phase.

Phase diagrams of the MeOH/EBBA and DBE/EBBA systems determined by the polarizing microscope (P.M.) are shown in Figure 2. The transition temperatures from solid to nematic and from nematic to isotropic phases were determined to be 39.0°C and 78.9°C, respectively. These are close to the reported values. The plots of N–N/I and N/I–I transition temperature vs. mole fraction of solute (X) give straight lines up to high mole fraction of solute in both systems. The boundary lines in MeOH/EBBA system are linear up to a mole fraction of ca. 0.4. Over this mole fraction, a noticeable drop in transition temperature is observed. The boundary lines in DBA/EBBA system show sharper decrease in transition temperature than those of MeOH/EBBA. This difference of the concentration dependence of the boundary lines in the two systems could be explained by the molecular volume of added solute. Since the molecular volume of MeOH is smaller than that of DBE, it can be presumed that the solute molecule dissolves without disordering the alignment of the liquid crystal even at higher mole fraction of solute in MeOH/EBBA system.

The reduced temperature (T^*) plots vs. X determined by P.M. for each system are shown in Figure 3. It is found that the plots of T^* vs. X give straight lines for each system. In theory, the extrapolated value of the T^* at $X = 0$ should be equal to 1. The experimental extrapolated value for each system varies only slightly from 1.

A theoretical treatment for this type of binary mixtures has been worked out by HJL. The expressions for the absolute values of the slopes of the lower line (β_n) and the upper line (β_i) are given by

$$\beta_n^\infty = \frac{\{\exp(0.418V_2/V_1) - 1\}}{0.418} \quad (1)$$

$$\beta_i^\infty = \frac{\{1 - \exp(-0.418V_2/V_1)\}}{0.418} \quad (2)$$

$$\frac{\beta_n^\infty}{\beta_i^\infty} = \frac{\gamma_n^\infty}{\gamma_i^\infty} = \exp(0.418V_2/V_1) \quad (3)$$

where V_1 and V_2 are the molecular volumes of a liquid crystal solvent and a spherical solute, respectively, the superscript ∞ designates the values at infinite dilution. Eqs. (1–3) are derived from the assumption that the value of interaction parameter between nematogen-solute equals zero.

The experimental values of β_n and β_i , the values of β_n^∞ and β_i^∞ calculated by the HJL's equations are given in Table I, where the value of V_2/V_1 is derived from the van der Waals volume.²¹ The agreement between the calculated and observed values is not highly satisfactory, though they agree

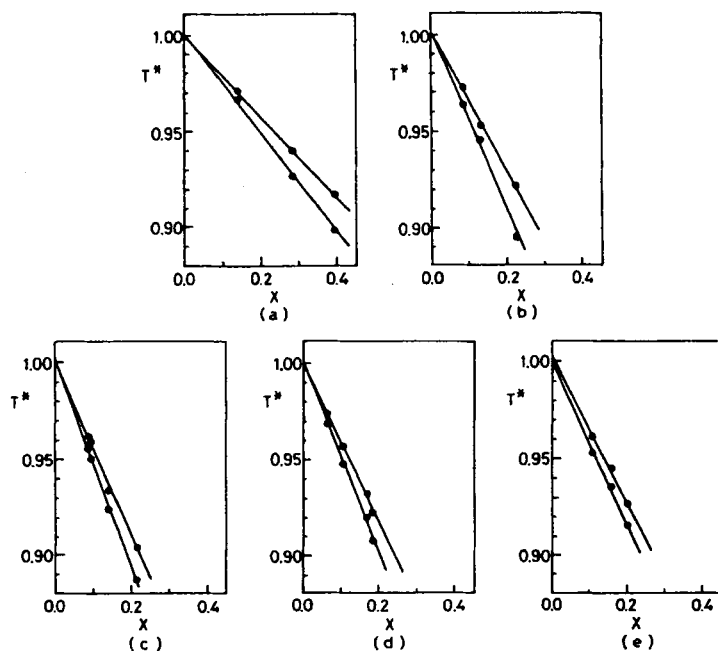


FIGURE 3 Diagrams of reduced temperature (T^*) vs. mole fraction of solute (X). (a) MeOH/EBBA; (b) DBE/EBBA; (c) *o*-X/EBBA; (d) *m*-X/EBBA; (e) *p*-X/EBBA.

qualitatively. When the nematogen-solute interaction is neglected, the orders of β_n 's and β_i 's can be predicted from the values of V_2/V_1 , since the values of β_n and β_i are directly proportional to the values of V_2/V_1 . As shown in Table I, the orders of β_n^∞ 's and β_i^∞ 's expected from V_2/V_1 are both MeOH < *c*-, *t*-DBE < *o*-, *m*-, *p*-X. The experimental results have the trend MeOH < DBE, *p*-X < *m*-X < *o*-X for β_n 's, and MeOH < DBE < *p*-X < *m*-X < *o*-X for β_i 's, respectively. This agrees qualitatively with the expected order of β_n and β_i .

TABLE I

The calculated values of β_n^∞ and β_i^∞ , and the experimental values of β_n and β_i .

solute	V_2/V_1	Calcd.			Obsd.		
		β_n^∞	β_i^∞	$\beta_n^\infty/\beta_i^\infty$	β_n	β_i	β_n/β_i
MeOH	0.12	0.123	0.117	1.05	0.26	0.21	1.23
DBE	0.26	0.275	0.246	1.11	0.41	0.35	1.17
<i>o</i> -X	0.42	0.459	0.385	1.19	0.53	0.46	1.17
<i>m</i> -X	0.42	0.459	0.385	1.19	0.49	0.42	1.19
<i>p</i> -X	0.42	0.459	0.385	1.19	0.41	0.38	1.10

The order of the experimental values of β_n and β_i for the xylene series with the same value of V_2/V_1 has the trend $o- > m- > p-X$. It may be pointed out that the values of β_n and β_i are dependent on the geometric shape of added solute molecule. The ratios of length-to-width for the solute molecules are in the order of $p- > m- > o-X$. This indicates that $p-X$ is more rod-like than the others, and thus dissolves easily in aligned EBBA. Consequently, it is assumed that the values of β_n and β_i for the $p-X$ /EBBA system are smaller than those of the others. Moreover, the geometric shape of added solute molecule may influence the interaction between the liquid crystal and an added solute.

2 $^1\text{H-NMR}$ spectra for partially oriented molecules

The order parameter of solute in the DBE/EBBA system Temperature dependence of the order parameter of the solute DBE was studied in the N and N/I phases. $^1\text{H-NMR}$ spectra were observed for the DBE/EBBA system at various concentrations (mole fractions of solute X = 0.08, 0.15, and 0.27). In the nematic phase of this system, the four signals due to oriented *c*-DBE and *t*-DBE (two from each) were observed on the broad background of EBBA. The direct coupling D_{HH} was estimated from the splitting ($\Delta\nu$) of each doublet signal for *c*-DBE and *t*-DBE. Thus, from measurement at a DBE (total) concentration, the values of the order parameter for *cis* and *trans* forms were determined separately. The order parameter S is derived from the equations,

$$\Delta\nu = |3 \cdot D_{HH}| \quad (4)$$

$$D_{HH} = - \frac{h\gamma^2}{4\pi^3 r^3} \cdot S \quad (5)$$

where γ is the gyromagnetic ratio of proton, r is the interproton distance (*c*-DBE: $r = 2.44\text{\AA}$, *t*-DBE: $r = 2.59\text{\AA}$), and h is the Planck's constant. The sign of S cannot be determined from $^1\text{H-NMR}$. Only the absolute value of the order parameter is discussed in this paper. Figure 4 shows the temperature dependence of the $|S|$ values for *c*-DBE and *t*-DBE in EBBA.

At both concentrations namely X = 0.08 and 0.15, the $|S|$ values for *c*-DBE decrease more rapidly with increasing temperature as compared with those for *t*-DBE. However, it can be seen from Figure 5 that although the magnitude of $|S|$ values for these solutes are quite different, the relative $|S|$ values decrease more or less in the same manner. The relative $|S|$ value here is the ratio of a $|S|$ value to the one measured at the lowest temperature (see Table II) in the nematic region. The relative temperature dependence of the order parameter of the solute depends only upon the solvent liquid

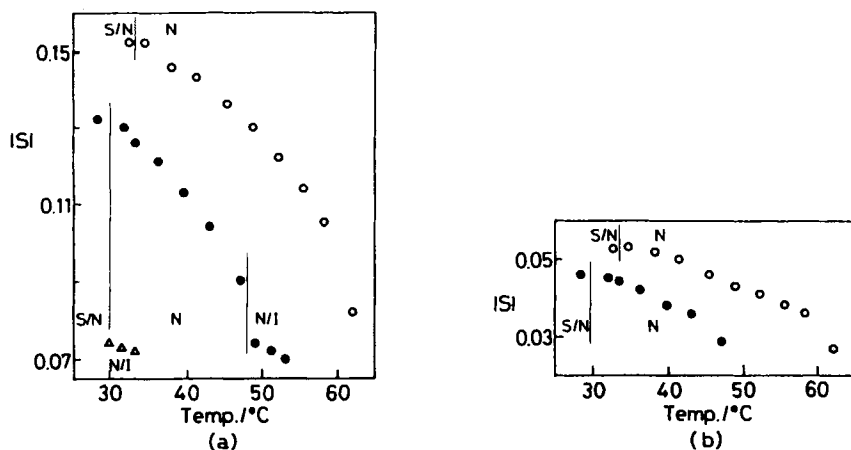


FIGURE 4 Temperature dependence of the $|S|$ values for *c*-DBE and *t*-DBE in EBBA. (a) *c*-DBE; (b) *t*-DBE \circ $X = 0.08$; \bullet $X = 0.15$; \triangle $X = 0.27$ X : total concentration.

crystal. This finding is in harmony with the observation in a nisoole azophenyl-*n*-capronate.⁷

The ^1H -NMR spectra of partially oriented *c*-DBE in N/I phase were observed at two total mole fractions, $X = 0.27$ and 0.15 . The signals from *trans* form in the nematic part could not be observed, since they were overlapped with the signals from the isotropic part of the solvent. The order

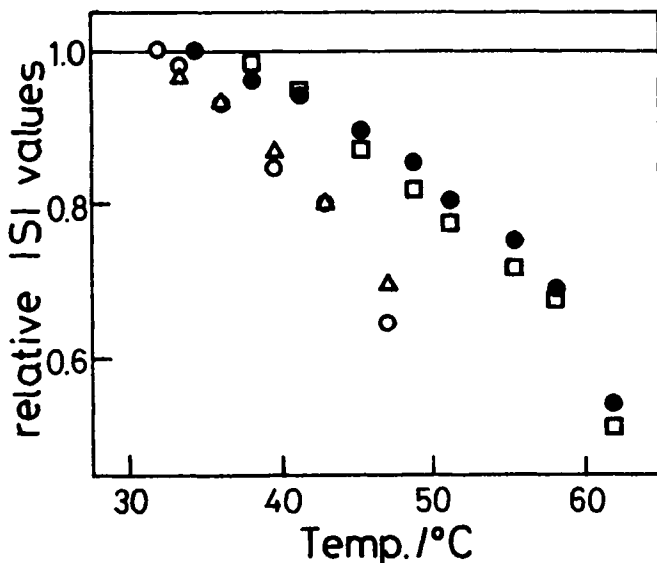


FIGURE 5 Temperature dependence of the relative $|S|$ values for *c*-DBE and *t*-DBE. $X = 0.08$: \bullet *c*-DBE; \square *t*-DBE $X = 0.15$; \circ *c*-DBE; \triangle *t*-DBE.

TABLE II
|S| values along H-H axis for *c*-DBE and *t*-DBE
in EBBA

X	Temp./°C	S value	
		<i>c</i> -DBE	<i>t</i> -DBE
0.08	34.6	0.152	0.053
0.15	31.9	0.130	0.045

parameter of these systems in this phase shows less temperature dependence compared with that in N phase. The magnitude of |S| in N/I phase is between 0.070 and 0.075. As shown in the phase diagram (see Figure 2), the mole fraction of added solute in the nematic part of N/I phase, which determines |S|, decreases with increase in temperature. The extent of alignment of a liquid crystal would increase with decreasing mole fraction of solute, while it would decrease with increasing temperature. Accordingly, in the nematic part the order parameter of the solute appears to be independent on temperature due to the cancellation of these two effects.

3 Proton spin-lattice relaxation time T_1 in MeOH/EBBA system

The height of the free induction decay M following the 90° pulse was measured as a function of τ . A plot of $\ln\{(M_0 - M)/M_0\}$ vs. τ yields a slope of $1/T_1$, where M_0 is the height of the free induction decay at very long τ or after a 90° pulse applied at thermal equilibrium.

The measurement of proton T_1 for MeOH/EBBA system was carried out at $X = 0.00, 0.30, 0.46$, and 0.60 . Figure 6 shows the temperature dependence of T_1 for MeOH/EBBA systems measured with increasing temperature. The S-N and N-I transitions of pure EBBA were monitored by observing decrease in T_1 . The S-N and N-I transition temperatures determined by T_1 measurements were 36°C and 78°C , respectively. These are good agreement with the values from polarizing microscope observation.

In the system of $X = 0.30$, this phase transition behaviour is different from that of pure EBBA due to the existence of N/I phase. In the temperature range of N/I coexisting phase (ca. 50°C - 60°C), T_1 does not change appreciably with temperature. Such temperature dependence of T_1 for MeOH/EBBA system of $X = 0.30$ is more prominent in the system of $X = 0.46$. In N/I range (35°C - 48°C) of this system, the measured values of T_1 remain almost constant within experimental error. It is thought that this phenomenon is due to two compensating effects, that is decrease in T_1 as the result of the

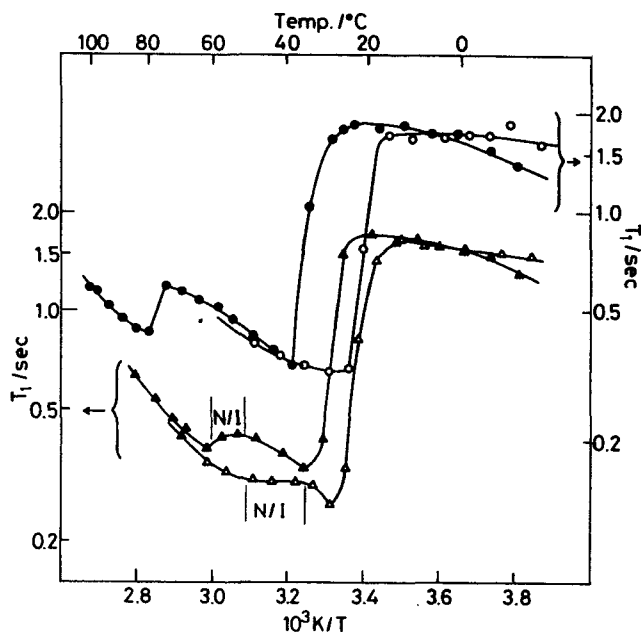


FIGURE 6 Temperature dependence of T_1 for MeOH/EBBA systems measured with increasing temperature. ● $X = 0.00$; ▲ $X = 0.30$; △ $X = 0.46$; ○ $X = 0.60$.

transition from nematic to isotropic part, and increase in T_1 in the nematic part with increase in temperature.

At $X = 0.60$, T_1 value increases monotonously over the transition temperature, since N and N/I phases are absent in this system.

CONCLUSIONS

The results of this work show the following: The slopes of the two boundary lines in binary systems can be qualitatively explained by HJL's formulae. On the discussion of the slopes, it is further necessary to take into account a liquid crystal-solute interaction. The relative temperature dependence of the order parameter of the added solute depends only upon the solvent liquid crystal in the nematic phase.

Temperature dependences of the order parameter and of the spin-lattice relaxation time in the nematic/isotropic coexisting phase indicate characteristic behaviour compared with those in nematic phase.

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