DIELECTRIC RELAXATIONS AND INTERMOLECULAR INTERACTION IN SEVERAL BINARY NEMATIC MIXTURES OF P-METHOXYBENZYLIDENE - P’-N-BUTYLANILINE AND NON-MESOGENIC COMPOUND

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DIELECTRIC RELAXATIONS AND INTERMOLECULAR INTERACTION
IN SEVERAL BINARY NEMATIC MIXTURES
OF P-METHOXYBENZYLIDENE — P'-N-BUTYLANILINE
AND NON-MESOGENIC COMPOUND

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1. Introduction. — The study on intermolecular interaction in nematic liquid crystals has been one of the most important problems among workers on nematic liquid crystals during the past decade, because the physical specificities of nematic liquid crystals essentially originate in the anisotropic intermolecular interaction in the nematic phase [1].

Recently, intermolecular interaction of binary nematic mixtures has been studied by several workers [2-6]. Binary nematic mixtures are divided briefly into two categories, nematic — nematic compound system and nematic — non-mesogenic compound system. The former systems frequently exhibit a phase diagram with a eutectic point. The curve connecting $T_{N+C\rightarrow N}$ and concentration of solute was thermodynamically explained by the Schroeder van Laar eq. [2]. Here, $T_{N+C\rightarrow N}$ is a transition temperature, at which nematic + crystals phase changes to nematic phase. So, the eutectic mixing ratio can be determined. On the other hand, changes of $T_{N+N+1}$ and $T_{N+1+1}$ with solute concentration are not so straightforwardly explained, and recently it was indicated by the lattice model theory [3], the virial expansion theory [4] and the HJL theory [5] that these transition temperatures were related to an intermolecular interaction between solvent and solute molecule. $T_{N-N+1}$ and $T_{N+1-1}$ are a transition temperature from nematic to nematic + isotropic phase and that from nematic + isotropic to isotropic phase, respectively. These theories predict that the shape of solute molecule play an important role in an intermolecular interaction. The intermolecular interaction increases with increasing the ratio of the molecular length along the long molecular axis to the diameter of the short molecular axis. The intermolecular interaction is connected to activity coefficient of solute in nematic mixtures, which can be measured by glc and NMR methods. Therefore, it is worthy to estimate the intermolecular interaction in the nematic mixtures by determining the activity coefficients from phase diagram, glc and NMR results. However, it must be pointed out that application of the three theories is restricted to a dilute concentration region of solute.

It is well known [7] that oriented nematic liquid crystals have two anisotropic dielectric relaxations, $H$-relaxation in the higher frequency and $L$-relaxation in the lower frequency. Meier and Sauge [8, 9] explained theoretically the mechanisms of the two dielectric relaxations by assuming that the $H$-relaxation is
due to the molecular rotational motion around the long molecular axis of nematic molecules, and that the L-relaxation is caused by a tumbling motion around the short molecular axis hindered by the long range — intermolecular interaction of nematic ordering. They derived the following relation between the relaxation time for the H-relaxation, $\tau_H$, and that for the L-relaxation, $\tau_L$

$$\tau_L/\tau_H = kT/q \exp(q/kT - 1) = kT/q \exp(q/kT).$$

(1)

Here, $k$ and $T$ are the Boltzmann constant and absolute temperature, respectively. $q$ is a potential barrier for the long range — intermolecular interaction of nematic ordering, i.e. nematic potential. By applying the Arrhenius equation to $\tau_L$ and $\tau_H$, the following equation is obtained

$$q = \Delta H_L - \Delta H_H.$$  

(2)

Therefore, $q$ can be obtained from $\Delta H_L$ and $\Delta H_H$. $\Delta H_L$ and $\Delta H_H$ are the activation enthalpy for the L-relaxation and that for the H-relaxation, respectively.

In previous papers [10, 11], we discussed whether an intermolecular interaction in binary nematic mixtures could be evaluated from anisotropic dielectric relaxations which were closely related to the nematic ordering in nematic liquid crystals, by using the eq. (2). We concluded that the dielectric method was very useful for estimation of an intermolecular interaction and that the Meier-Saupe theory held well in binary nematic mixtures.

The purpose of this paper is to clarify an intermolecular interaction in binary nematic mixtures of p-methoxybenzylidene — p'-n-butylaniline (MBBA) and non-mesogenic compounds by studying their dielectric relaxations. Non-mesogenic compounds used here are non-linear shaped molecules such as chloroform, m-xylene and 1,3,5-trimethylbenzene, and nearly linear shaped molecules such as p-nbutylanilene, p-xylene and azobenzene.

2. Experimental. — MBBA was synthesized and purified by the same procedure as was described previously [11]. Chloroform, p-xylene, m-xylene and 1,3,5-trimethylbenzene were distilled just before use. Azobenzene was recrystallized from absolute ethanol.

Dielectric and viscosity measurements were made by the same methods as were described previously [11]. Dielectric constant, $\varepsilon'_1$, and the loss, $\varepsilon''_1$, in the parallel direction to the applied magnetic field of 4 000 Oe, were measured in the frequency range of 300 Hz to 3 MHz in the nematic state.

3. Results and discussion. — Figures 1a and b show frequency dependence of $\varepsilon'_1$ and $\varepsilon''_1$ for MBBA — azobenzene system, where mole % of azobenzene is 5.0, at several temperatures. The L-relaxation is observed in MHz regions. The L-relaxations were also observed for all the other systems used here. Figure 2 shows the Arrhenius plots of logarithmus of $\tau_L$ against $1/T$ for all the systems. The values of $\Delta H_L$ and $\Delta S_L$ are listed in table I. The values of $\tau_L$ decreased when non-mesogenic compound was added to MBBA. In the previous paper [11], we concluded that the values of $\tau_L$ increased with the increase of additive concentration when additive was nematoenic compound, and vise vira when additive was non-mesogenic compound. These data support the previous conclusion.

Figure 3 shows the Arrhenius plots of logarithmus of viscosity at the isotropic phase, log $\eta$, against $1/T$ for all the systems, and the values of activation enthalpy, $\Delta H_p$, obtained from the slope are listed in table I. Although $\eta$ is not always proportional to $\tau_H$ quantitatively, we assumed $\Delta H_p = \Delta H_L$ in the eq. (2). The values of $q$ obtained are also listed in table I. Evidently, all the systems have the same value of $\Delta H_p$ as that of MBBA, whereas the values of $\Delta H_L$ for systems where linear shaped molecules

<table>
<thead>
<tr>
<th>Non-mesogenic compound</th>
<th>Shape of molecule</th>
<th>Concentration of solute mole %</th>
<th>Conductivity $\Omega^{-1} \cdot \text{cm}^{-1}$ at 25°C</th>
<th>$\tau_L$ s (10^{-8})</th>
<th>$\Delta H_L$ kJ/mole</th>
<th>$\Delta S_L$ J/mole deg</th>
<th>$\Delta H_p$ kJ/mole</th>
<th>$q$ kJ/mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloroform</td>
<td>non-linear</td>
<td>3.7</td>
<td>0.16</td>
<td>10.3</td>
<td>63.2</td>
<td>100</td>
<td>28.0</td>
<td>35.2</td>
</tr>
<tr>
<td>p-n-butylanilene</td>
<td>nearly linear</td>
<td>4.8</td>
<td>2.0</td>
<td>6.55</td>
<td>61.9</td>
<td>99.1</td>
<td>26.4</td>
<td>41.8</td>
</tr>
<tr>
<td>p-xylene</td>
<td>nearly linear</td>
<td>2.0</td>
<td>1.6</td>
<td>5.97</td>
<td>68.2</td>
<td>121</td>
<td>26.8</td>
<td>53.9</td>
</tr>
<tr>
<td>m-xylene</td>
<td>non-linear</td>
<td>2.0</td>
<td>0.82</td>
<td>4.58</td>
<td>88.3</td>
<td>191</td>
<td>24.7</td>
<td>63.6</td>
</tr>
<tr>
<td>Azobenzene</td>
<td>nearly linear</td>
<td>5.0</td>
<td>1.3</td>
<td>7.36</td>
<td>64.8</td>
<td>107</td>
<td>26.8</td>
<td>38.0</td>
</tr>
<tr>
<td>1,3,5-trimethylbenzene</td>
<td>non-linear</td>
<td>8.0</td>
<td>0.61</td>
<td>4.66</td>
<td>64.4</td>
<td>110</td>
<td>25.1</td>
<td>39.3</td>
</tr>
</tbody>
</table>

Table I

Activation parameters for L-relaxations in various binary nematic mixtures of MBBA and non-mesogenic compound
were used, are larger than those for MBBA. Therefore, the values of \( g \) were larger when the linear shaped molecules were added, and was constant when non-linear shaped molecules were added. These results mean that linear shaped molecules strengthen a long range — intermolecular interaction in nematic mixtures, and do not give any effect on a short range — intermolecular interaction, and that non-linear shaped molecules do not play any role in both intermolecular interactions in nematic mixtures. The above results seem to be consistent with the HJL theory, the lattice model theory and the virial expansion theory; (a) These theories concern mainly with an intermolecular interaction between nematic solvent and solute. In contrast, the dielectric results can detect an intermolecular interaction of nematic ordering and can indicate the presence of an effect of solute on the nematic ordering of nematic solvent itself, MBBA in this study. (b) In fact, any effect of non-linear shaped solute on intermolecular interaction in nematic mixtures was not observed in the present study. (c) This fact suggest that an intermolecular interaction between nematic solvent and non-linear shaped solute is not larger than that between solvent and solvent, which is expected by the three theories. It must be emphasized, anyhow, that non-mesogenic linear molecules strengthen only a long range — intermolecular interaction and not a short...
range — intermolecular interaction. Our previous results [11] on MBBA — p-ethoxybenzylidene — p’-cyanoaniline (EBCA) system, which has a eutectic point in the phase diagram, indicated that both a long range — and a short range — intermolecular interaction increased anomalously at the vicinity of the eutectic mixing ratio. Of course, EBCA is a rigid and lathlike molecule, i.e. a linear and nemato-
genic molecule. Consequently, it is valid that the linear molecules strengthen an intermolecular interaction in nematic ordering.

Figure 4 shows plots of $\tau_L$ against $\eta$ for several systems of MBBA — non-mesogenic and non-linear shaped compound at 49.3 °C. Clearly, the values of $\tau_L$ change linearly with the values of $\eta$ in MBBA — non-linear compound systems. A linear equation,

$$\tau_L (s) = -3.2 \times 10^{-8} + 4.0 \times 10^{-9} \eta \text{ (C.P.)},$$

was obtained in MBBA — non-linear compound systems. It seems to contradict the Debye eq. [13] that $\eta = 8.2$ C.P. when $\tau_L = 0$. However, this may suggest that the nematic phase disappears at $\eta = 8.2$ ($\tau_L = 0$). When the linear shaped molecules were used, data were not plotted on the above straight line, due to the change of $\Delta H_L$ by additives. However, the change of $\tau_L$ by mixing additives depends rather on $\eta$ than $\eta$, as described in the previous paper.

In conclusion, an intermolecular interaction in nematic mixtures may be influenced by the molecular shape of solute; the linear shaped solute strengthen a long range — intermolecular interaction in nematic ordering, but the non-linear shaped solute do not have any influence on intermolecular interaction. We can state that the dielectric study provides us with interesting information on intermolecular interaction in nematic mixtures.

References