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Thermodynamic Effect on Viscosity and Density of a Mixture of 4-Cyano-4'-pentylbiphenyl (5CB) with Dilute Dimethyl Phthalate (DMP)

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Density ρ and viscosity η were examined for 4-cyano-4'-pentylbiphenyl (5CB) and its mixture with dilute dimethyl phthalate (DMP; $w_{\text{DMP}} = 3.1$ wt%). The mixture was in an isotropic 1-phase state at temperatures $T > T_{\text{IN}}^*$ ($\cong 27^\circ\text{C}$), and exhibited the phase separation into the isotropic and nematic phases at T_{IN}^* . Pure 5CB exhibited the (well known) first-order isotropic-to-nematic transition characterized by discontinuous changes of ρ and η at T_{IN} ($\cong 35.0^\circ\text{C}$), whereas no discontinuous changes were observed for the mixture at T_{IN}^* because only a small amount of the nematic phase was created at T_{IN}^* . The discontinuity was expected for the *local* density and viscosity in the nematic phase at T_{IN}^* and, in this sense, no essential difference was noted for that phase in the 5CB and DMP/5CB systems. Nevertheless, a characteristic difference was found in the isotropic 1-phase state. These systems commonly exhibited simple asymptotic behavior at sufficiently high T , linear thermal expansion of the specific volume $1/\rho$ and Eyring/Andrade-type T dependence of the kinematic viscosity, $\nu = \eta/\rho$. Positive deviation from these asymptotes was noted for both systems on cooling toward respective transition temperatures, T_{IN} and T_{IN}^* , but in a considerably wide range of T (up to $T_{\text{IN}}^* + 10\text{K}$ or more) for the DMP/5CB mixture whereas only in a close vicinity of T_{IN} (within a few K) for pure 5CB. This difference is related to the concentration fluctuation (due to the soft, osmotic interaction of molecules) emerging only in the mixture.

Key Words: DMP-5CB mixture / Viscosity / Density / Isotropic-to-nematic transition / Concentration fluctuation

1. INTRODUCTION

Rheological behavior of liquid crystalline (LC) materials has been a subject of extensive research in the softmatter community. The LC molecules have well-defined order parameters, and the free energy of the system can be expressed in terms of the order parameters and accordingly the stress is related to those parameters¹⁻³⁾. This expression allows rheological investigation of the molecular dynamics in LC systems. For example, oscillation of the stress on start-up of shear flow, observed for 4-cyano-4'-*n*-octylbiphenyl (8CB) in the nematic state, is related to the tumbling dynamics of 8CB molecules²⁾.

LC molecules also offer a rich field of research when mixed with non-LC molecules, either polymers or low molecular weight (low- M) solvents, because the free energy of the mixture determining the phase behavior and molecular dynamics is contributed not only from the LC free energy expressed in terms of the order parameters but also from the

mixing free energy not directly related to those parameters⁴⁻⁶⁾. This free energy has been utilized to discuss complicated phase evolution in LC/polymer mixtures⁴⁾ and in LC/low- M solvent mixtures^{5,6)}. A characteristic feature of these mixtures is the coupling between the LC free energy and the mixing free energy that allows the LC transition to trigger the phase separation (mostly *via* spinodal decomposition) and *vice versa*. Correspondingly, the molecular dynamics in the LC phase is tuned by this coupling.

This coupling is expected to affect properties of the LC/non-LC mixtures even in the isotropic 1-phase state, but details of this effect have not been well elucidated. Thus, in this study, we attempt to *experimentally* resolve the effect on the static (thermodynamic) and kinetic (rheological) properties in the isotropic 1-phase state. For this purpose, we focused on a mixture of 4-cyano-4'-pentylbiphenyl (5CB) with a small amount of dimethyl phthalate (DMP; $w_{\text{DMP}} = 3.1$ wt%). Utilizing the pure 5CB system as a reference, we examined the mass density ρ and zero-shear viscosity η of the mixture. At sufficiently high temperatures T , both 5CB and DMP/5CB systems were in the isotropic 1-phase state and exhibited simple asymptotic behavior, linear thermal expansion of the

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specific volume $1/\rho$ and the Eyring/Andrade-type T dependence of the kinematic viscosity, $\nu = \eta/\rho$. Positive deviation from these high- T asymptotes was noted for both 5CB and DMP/5CB systems on a decrease of T toward respective isotropic-to-nematic transition temperatures, T_{IN} and T_{IN}^* , but only in a close vicinity of T_{IN} (within a few K) for pure 5CB whereas in a considerably wider range of T above T_{IN}^* (within 10K or more) for the DMP/5CB system. This difference is related to a soft, *osmotic* interaction of molecules in the DMP/5CB system (not existing in the pure 5CB system), which should correspond to the contribution of the mixing free energy to ρ and ν of the mixture in the isotropic 1-phase state. Details of these results are presented in this article.

2. EXPERIMENTAL

2-1 Materials

Commercially available 4-cyano-4'-pentylbiphenyl (5CB; purity > 98.0 %; Tokyo Chemical Industry Co. Ltd) and dimethyl phthalate (DMP; guaranteed grade; FujiFilm Wako Pure Chemical Corp.) were used as received. A DMP/5CB mixture with the DMP weight fraction of $w_{\text{DMP}} = 3.1$ wt% was prepared by mechanically mixing prescribed masses of DMP and 5CB at 40 °C. (DMP and 5CB were highly miscible at 40 °C and almost instantaneously mixed with each other.) This mixture, pure 5CB, and pure DMP were degassed prior to the measurements explained below.

2-2 Determination of Phase Transition Temperature

The DMP/5CB mixture and pure 5CB were charged in glass tubes and mechanically stirred in a T -controlled water bath. After keeping these samples quiescently for ≥ 12 h at a given T , we visually examined their transparency to determine the phase transition temperature(s). In addition, a cross-polarized optical microscope (BX53, Olympus Corporation) was utilized to detect a nematic phase in each sample kept on a T -controlled stage (LK-600PM, Linkam; Japan High Tech Co. Ltd). With these methods, the isotropic-to-nematic (IN) transition temperature, $T_{\text{IN}} \cong 35.0$ °C for pure 5CB and $T_{\text{IN}}^* \cong 27.0$ °C for the DMP/5CB mixture, were determined within an accuracy of the temperature control (within 0.1 °C). T_{IN}^* for the DMP/5CB mixture was the temperature for the onset of phase separation into nematic and isotropic phases on cooling, and the mixture exhibited another transition, full conversion into the nematic phase (disappearance of the isotropic phase), at $T_{\text{IN}}^{**} \cong 22.5$ °C.

2-3 Density Measurement

The mass density of the DMP/5CB mixture ($w_{\text{DMP}} = 3.1$ wt%) was measured at $T = 19$ -50 °C with a densitometer (DA-640, Kyoto Electronics Manufacturing Co., Ltd.). This densitometer detects the mechanical impedance of a U-shaped glass tube filled with a sample and converts the impedance into the sample density. The DMP/5CB mixture was kept/equilibrated at each test temperature (controlled within 0.1 °C) for 20-30 min before each run of the measurement. The density was measured in the same way also for pure 5CB and pure DMP.

2-4 Viscosity Measurement

The zero-shear viscosity of the DMP/5CB mixture was measured at $T = 15$ -56 °C with a viscometer (EMS-1000S, Kyoto Electronics Manufacturing Co., Ltd.). This viscometer drives a small aluminum ball electromagnetically to detect the rotating speed of the ball, and converts this speed into the sample viscosity. The shear rate $\dot{\gamma}$ corresponding to this rotating speed was kept small ($\dot{\gamma} < 100$ s⁻¹) to ensure that the zero-shear viscosity was obtained. (The relaxation frequency estimated from a separate dielectric test was larger than 10⁶ s⁻¹, which guaranteed the zero-shear response at $\dot{\gamma} < 100$ s⁻¹.) The DMP/5CB mixture was quiescently equilibrated at each test temperature (controlled within 0.1 °C) for 20-30 min before each run the measurement. The viscosity was measured in the same way also for pure 5CB and pure DMP.

3. RESULTS AND DISCUSSION

3-1 Phase Transition Temperature

For the DMP/5CB mixture ($w_{\text{DMP}} = 3.1$ wt%) charged in a glass tube, Fig. 1 shows typical results of visual observation of the phase behavior. The mixture, soaked in a temperature-controlled water bath, was mechanically stirred for ~30 min and then kept quiescently for ≥ 12 h to equilibrate the phase state. As seen in Fig. 1, the mixture after this equilibration was transparent and in the 1-phase isotropic state at $T > 27.0$ °C, although it became slightly hazy (due to the concentration fluctuation) in a vicinity of 27.0 °C; see the photo at 30.0 °C. On cooling to 27.0 °C, the mixture just after the stirring (shown in Fig. 1) became opaque, indicating that the isotropic-to-nematic (IN) transition temperature of the mixture was $T_{\text{IN}}^* \cong 27.0$ °C (After the 12 h equilibration, no detectable amount of the nematic phase precipitated. Thus, a photo in that state is not shown in Fig. 1.). Appearance of the nematic phase at this T_{IN}^* was also confirmed from the

Fig. 1 Visual observation of phase behavior of DMP/5CB mixture ($w_{\text{DMP}} = 3.1$ wt%).

cross-polarized optical microscope observation.

At lower T , 26.0 °C, the mixture after the equilibration was macroscopically separated into a transparent isotropic phase and an opaque nematic phase (the opaque phase was confirmed to be in the nematic state with the aid of the cross-polarized optical microscopy), indicating that the IN transition of the mixture was associated with the phase separation. Finally, the isotropic phase disappeared and the whole mixture was converted into the 1-phase nematic state after the equilibration at the second transition temperature, $T_{\text{IN}}^{**} \cong 22.5$ °C. These T_{IN}^* and T_{IN}^{**} , determined within an accuracy of the temperature control (within 0.1 °C), serve as important reference temperatures in our later discussion of the density and viscosity data.

For comparison, the phase behavior was similarly examined for pure 5CB. We confirmed that pure 5CB exhibits the IN transition at $T_{\text{IN}} \cong 35.0$ °C. The isotropic phase of pure 5CB was fully converted into the nematic phase at $T < T_{\text{IN}}$ (which differed from the phase separation behavior of the DMP/5CB mixture). This observation agrees with the behavior of bulk 5CB reported in literature, with the reported T_{IN} being in a range of 34.0-35.3 °C⁷⁻¹¹.

3-2 Density

Figure 2 shows changes of the mass density ρ with temperature T measured for the DMP/5CB mixture with $w_{\text{DMP}} = 3.1$ wt% (red circle), pure 5CB (green square), and pure DMP (black diamond referring to the right vertical axis). Unfilled and filled symbols indicate that the material was in the 1-phase isotropic and nematic state, respectively, and the red circle with an inner dot specifies the DMP/5CB mixture separated into the isotropic and nematic phases.

Pure DMP is a simple, isotropic liquid in the entire range of T examined, and a decrease of its ρ on an increase of T is

Fig. 2 Changes of mass density with temperature measured for DMP/5CB mixture ($w_{\text{DMP}} = 3.1$ wt%), pure 5CB, and pure DMP. Unfilled and filled symbols indicate that the material was in the 1-phase isotropic and nematic state, respectively, and the red circle with an inner dot specifies the DMP/5CB mixture separated into isotropic and nematic phases. Black double-headed arrow highlights a discontinuous change of the density of pure 5CB at T_{IN} .

essentially linear with respect to T , as expected for simple thermal expansion. In contrast, pure 5CB is in the 1-phase nematic and isotropic states at T below and above T_{NI} ($\cong 35.0$ °C), respectively, and exhibits a discontinuous change of ρ at T_{NI} ; cf. black two-headed arrow attached to green squares. This discontinuity is characteristic to the first-order thermodynamic transition (NI transition)^{1, 3}. Despite this discontinuity, pure 5CB exhibits simple thermal expansion at T well below and well above T_{NI} , as noted from the change of ρ being almost linear with respect to T in those low- and high- T zones. (Pure 5CB is supposed to crystallize at 22-24 °C^{11, 12}), but is easily super-cooled to stay in the nematic state even at T well below 24 °C. The simple thermal expansion seen at $T < 24$ °C is the behavior of this super-cooled nematic 5CB.)

Differing from pure 5CB, the DMP/5CB mixture exhibits no discontinuous change of ρ at its isotropic-to-nematic transition temperature T_{NI}^* ($\cong 27.0$ °C); see the continuity between the unfilled circles and the circles with inner dots. Similar behavior has been noted for mixtures of 5CB with ethanol⁶) and tetraethylmethane⁷). This lack of discontinuity reflects the phase separation occurring together with the IN transition. Namely, at T_{NI}^* , the nematic phase is formed but its volume fraction ϕ_{N} is very small so that ρ of the mixture

coincides with ρ of the isotropic phase. This ϕ_N gradually increases from 0 to 1 on a decrease of T from T_{NI}^* to T_{NI}^{**} ($\cong 22.5^\circ\text{C}$), as can be noted from Fig. 1. This gradual increase of ϕ_N results in a continuous increase of ρ at those T , as noted for the circles with inner dots in Fig. 2. Finally, at $T < T_{NI}^{**}$, the mixture is in the 1-phase nematic state and its ρ keeps increasing continuously in a way similar to the behavior of the nematic phase of pure 5CB. The *local* density of the nematic phase in the mixture would have exhibited a discontinuity on a decrease of T below T_{NI}^* , but this discontinuity is smeared for the mixture as a whole due to the gradual change of ϕ_N . In this sense (regarding the nematic phase), no essential difference is expected for the 5CB and DMP/5CB systems.

In Fig. 2, we also note that the T dependence of ρ at sufficiently high and low T is similar for the pure DMP, pure 5CB, and DMP/5CB systems. In fact, this dependence is in accord to the simple, linear thermal expansion of the specific volume v_{sp} described by

$$v_{sp}(T) = v_{sp}^\circ + \alpha T \quad (T \text{ in } ^\circ\text{C}) \quad (1)$$

$$\rho(T) = 1/v_{sp}(T) \quad (2)$$

With the specific volume v_{sp}° at a hypothetical reference state (0°C) and the thermal expansion coefficient α summarized in Table I, eqs 1 and 2 excellently fit the ρ data at high and low T in Fig. 2; see the black, green, and red lines for the pure DMP, pure 5CB, and DMP/5CB systems, respectively.

If the DMP and 5CB molecules exhibit no *extra* interaction specific to the mixture (the interaction not emerging in respective pure systems), a simple mixing rule shown below is expected to work for the density of the DMP/5CB mixture in 1-phase state.

$$\rho_{\text{DMP/5CB}}^{\text{simple mixing}}(T) = \frac{1}{w_{\text{DMP}} v_{sp}^{\text{DMP}}(T) + \{1 - w_{\text{DMP}}\} v_{sp}^{\text{5CB}}(T)} \quad (3)$$

Here, $v_{sp}^{\text{DMP}}(T)$ and $v_{sp}^{\text{5CB}}(T)$ are the specific volumes of pure DMP and 5CB described by eqs 1 and 2 with the parameters

Table I Parameters for simple thermal expansion of specific volume.

system	$v_{sp}^\circ / \text{cm}^3 \text{ g}^{-1}$	$10^4 \alpha / \text{cm}^3 \text{ g}^{-1} \text{ K}^{-1}$
pure DMP at all T	0.8259	6.7
pure 5CB	at high T	0.9639
	at low T	0.9577
DMP/5CB	at high T	0.9616
	at low T	0.9544

given in Table I, and w_{DMP} ($= 0.031$) is the DMP weight fraction in the mixture. In Fig. 2, the dotted blue lines at high and low T show $0.9992\rho_{\text{DMP/5CB}}^{\text{simple mixing}}(T)$ and $0.9977\rho_{\text{DMP/5CB}}^{\text{simple mixing}}(T)$ that are calculated from eq 3 at respective T and slightly adjusted by a factor $< 0.3\%$ (as shown by the numerical front factors). These calculated lines describe the ρ data of the mixture at high and low T (unfilled and filled red circles) surprisingly well. This result suggests that the DMP and 5CB molecules in the mixture exhibit no extra interaction specific to the mixture. In this sense, the 5CB and DMP/5CB systems exhibit no essential difference in their density at high and low T .

Nevertheless, for these systems, we note a delicate but important difference in the deviation from the high- T asymptote of the density of the isotropic phase, $\rho^{\text{iso-high } T}(T)$ calculated from eqs 1 and 2 at respective T with the parameters shown in Table I. This difference is demonstrated in Fig. 3 where the deviation from the high- T asymptote, $\Delta\rho = \rho(T) - \rho^{\text{iso-high } T}(T)$, is normalized by $\rho^{\text{iso-high } T}(T)$ of each material and plotted against T . For pure DMP (Fig. 3c), $\Delta\rho/\rho^{\text{iso-high } T} = 0$ in the entire range of T , confirming that DMP is a thermodynamically simple liquid showing the linear thermal expansion of the specific volume (cf. eqs 1 and 2).

In contrast, for both DMP/5CB mixture and pure 5CB systems in the 1-phase isotropic state (unfilled symbols in Figs. 3b and 3a), $\Delta\rho/\rho^{\text{iso-high } T} = 0$ at sufficiently high T (by

Fig. 3 Changes of the normalized deviation of density, $\Delta\rho/\rho^{\text{iso-high } T}$ ($\Delta\rho = \rho - \rho^{\text{iso-high } T}$), with T observed for the DMP/5CB mixture ($w_{\text{DMP}} = 3.1 \text{ wt}\%$), pure 5CB, and pure DMP. The sense of the symbols is the same as in Fig. 2. Black double-headed arrow highlights a discontinuous jump of $\Delta\rho/\rho^{\text{iso-high } T}$ of pure 5CB at T_{IN} .

definition) but a positive deviation from this high- T asymptote by a factor of $\sim 0.03\%$ ($\Delta\rho/\rho^{\text{iso-high } T} \cong 0.0003$) is noted on a decrease of T toward the IN transition temperature, T_{IN} and/or T_{NI}^* . Because the maximum increase of the $\Delta\rho/\rho^{\text{iso-high } T}$ ratio in the entire range of T is below 0.6% , the deviation by a factor of $\sim 0.03\%$ is not trivial at all. For the pure 5CB system, this deviation is observed only in a close vicinity of T_{IN} (within 1 K before the $\Delta\rho/\rho^{\text{iso-high } T}$ ratio exhibits the discontinuous jump at T_{IN}); see unfilled green squares. In contrast, the deviation for the DMP/5CB mixture emerges gradually over a much wider range of T between T_{IN} and $T_{\text{IN}}+10\text{K}$; see unfilled red circles.

The positive deviation of $\Delta\rho/\rho^{\text{iso-high } T}$, indicating an extra densification of the *isotropic* phase near the IN transition point, can be related to an extra correlation of molecules in the vicinity of the transition point. In the pure 5CB system, this correlation is related to the bulk compressibility and reflected in the density fluctuation the 5CB molecule. In contrast, in the DMP/5CB mixture, the correlation is mostly related to the osmotic compressibility and reflected in the concentration fluctuation (in addition to the density fluctuation). The concentration fluctuation, not existing in the pure 5CB system, appears to be the factor that gives rise to the above gradual deviation of $\Delta\rho/\rho^{\text{iso-high } T}$ in the wide range of T . This effect of the concentration fluctuation (*i.e.*, an osmotic effect) is further discussed later in relation to the viscosity data.

3-3 Viscosity

For the DMP/5CB mixture ($w_{\text{DMP}} = 3.1\text{ wt}\%$) and the pure 5CB and DMP systems, Fig. 4 shows plots of the zero-shear viscosity η against $1000T^{-1}$ (T in unit of K). Pure DMP behaves just as a simple viscous fluid, whereas pure 5CB exhibits a discontinuous decrease of η on the IN transition at T_{IN} . This discontinuity of η , corresponding to that seen for the density (Fig. 2), is characteristic to nematic LC^{1-3, 13} exhibiting the first-order IN transition. In the nematic state, η of 5CB is strongly dependent on the LC texture being sensitive to shear flow, and the viscosity is known to change with the relative alignment of the LC director with respect to the flow^{1-3, 13}. The gradual decrease of η followed by an increase noted for our pure 5CB system on a decrease of $T < T_{\text{IN}}$ (filled green squares) should reflect the dynamics of such a texture that changes with T .

The DMP/5CB mixture does not exhibit the discontinuity of η on the IN transition at T_{IN}^* because of the phase separation occurring simultaneously. As discussed for the density (Fig. 2), the volume fraction of the nematic phase ϕ_{N}

Fig. 4 Zero-shear viscosity η measured for DMP/5CB mixture ($w_{\text{DMP}} = 3.1\text{ wt}\%$) and pure 5CB and DMP. The sense of the symbols is the same as in Fig. 2.

increases from 0 to 1 on a decrease of T from T_{IN}^* to T_{IN}^{**} ($\cong 22.5^\circ\text{C}$) so that the discontinuity expected for the *local* viscosity of the nematic phase at T_{IN}^* would have been smeared for the mixture as a whole. In this sense (regarding the nematic phase), we again note no essential difference between the pure 5CB system and the DMP/5CB mixture.

Following the strategy explained for Fig. 3, we here focus on the viscosity of the pure 5CB and DMP/5CB systems in the *isotropic 1-phase state* in the vicinity of T_{IN} and/or T_{IN}^* to examine if a characteristic difference is noted for these systems. For this purpose, it is informative to consider the well-established statistical expression of the zero-shear viscosity η of a simple fluid. Under shear flow in x direction with a shear gradient in y direction, η is expressed in terms of the position $\mathbf{r}_i$ and the velocity $\mathbf{v}_i$ of i -th particle (atom or molecule) in the fluid and the total inter-particle force $\mathbf{F}_i$ acting on this particle^{14, 15}:

$$\eta = \frac{1}{Vk_{\text{B}}T} \int_0^\infty \sum_{i,j=1}^N \langle J_i(t) J_j(0) \rangle_{\text{eq}} dt \quad (4)$$

with

$$J_i(t) = \frac{p_{ix}(t)p_{iy}(t)}{m} + x_i(t)F_{iy}(t) \quad (5)$$

Here, x_i is the x -component of $\mathbf{r}_i$, m and $p_{i,\xi} = mv_{i,\xi}$ ($\xi = x, y$) are the mass and the ξ -component of the momentum of the particle i , F_{iy} is the y -component of $\mathbf{F}_i$, N is the total number of the particles in a volume V , and $\langle \cdots \rangle_{\text{eq}}$ indicates an ensemble average at equilibrium. k_{B} and T are the Boltzmann constant and absolute temperature, respectively. Equations 4 and 5 indicate that η is contributed from the momentum transport

and the inter-particle interaction. If η is dominantly contributed from this interaction (which seems to be the case for our 5CB and DMP/5CB systems having large $\eta > 10$ mPa s; cf. Fig. 4), the flux J_i can be expressed as $J_i \cong x_i F_{i,y}$. Then, eqs 4 and 5 become equivalent to the well-known Kramers expression of the shear stress σ ^{16, 17},

$$\sigma(t) = -\frac{1}{V} \sum_{i=1}^N \langle x_i(t) F_{i,y}(t) \rangle_{\text{under flow}} \quad (6)$$

In eq 6, the average $\langle \cdot \rangle_{\text{under flow}}$ is taken for the particles under flow (having a spatial distribution distorted by the flow).

The above expressions of η and $\sigma(t)$ suggest that the mass density ρ directly contributes to η and $\sigma(t)$ and thus the kinematic viscosity $\nu \equiv \eta/\rho$, not the viscosity η itself, includes direct information of the dynamics averaged for individual particles. Considering that the inter-particle interaction governs ν of our 5CB and DMP/5CB systems, we may rewrite eqs 4-6 as

$$\begin{aligned} \nu &= \frac{1}{mk_B T} \int_0^\infty \frac{1}{N} \sum_{i,j=1}^N \langle x_i(t) x_j(0) F_{i,y}(t) F_{j,y}(0) \rangle_{\text{eq}} dt \\ &= -\left(\frac{1}{m\dot{\gamma}} \right) \frac{1}{N} \sum_{i=1}^N \langle x_i F_{i,y} \rangle_{\text{under steady shear at } \dot{\gamma}} \end{aligned} \quad (7)$$

where the factor $N^{-1} \sum \langle \cdot \rangle$ shows the average for individual particles. Equation 7 indicates that the viscosity is enhanced if the inter-particle (inter-molecular) force is transmitted over a longer distance thereby correlating more particles (more molecules) located at that distance. This long-ranged inter-particle force enhances fluctuations of the density and concentration (and the orientation if the particles are not spherical). Namely, the stronger the correlation and fluctuation, the larger the viscosity. Following this argument, we reduced the η data of the DMP/5CB mixture, pure 5CB, and pure DMP (Fig. 4) by the ρ data (Fig. 2) at respective T to examine the temperature dependence of the kinematic viscosity, ν . The results are summarized in Fig. 5.

At sufficiently high T , the fluctuation discussed above should relax rapidly. Then, all systems examined in Fig. 5 are expected to exhibit the simple Eyring/Andrade-type behavior² of the kinematic viscosity,

$$\nu^{\text{iso-high } T}(T) = \nu^\infty \exp\left(\frac{E_a}{RT}\right) \quad (8)$$

with R being the gas constant. In fact, this expectation is confirmed, as shown in Fig. 5 with the solid lines calculated from eq 8 with the activation energy E_a and the limiting value of the kinematic viscosity ν^∞ summarized in Table II.

For pure 5CB, pure DMP, and the DMP/5CB mixture,

Fig. 5 Temperature dependence of the kinematic viscosity $\nu (= \eta/\rho)$ of pure 5CB, pure DMP, and DMP/5CB mixture ($w_{\text{DMP}} = 3.1$ wt%). Solid lines indicate the asymptotic Eyring/Andrade-type behavior in the isotropic 1-phase state at high T . The sense of the symbols is the same as in Fig. 2.

we examined the temperature dependence of the $\nu(T)$ data (Fig. 5) normalized by the high- T asymptote, $\nu^{\text{iso-high } T}(T)$ (eq 8 and Table II). For all systems, $\nu / \nu^{\text{iso-high } T} = 1$ at sufficiently high T (by definition) but a positive deviation from this high- T asymptote was observed on a decrease of T . For clear observation of this deviation, Fig. 6 shows plots of the normalized deviation, $\Delta\nu / \nu^{\text{iso-high } T}$ with $\Delta\nu = \nu - \nu^{\text{iso-high } T}$, against T .

Pure DMP behaves as a thermodynamically simple liquid showing the linear thermal expansion of the specific volume in the entire range of T , as confirmed in Fig. 3c. Consequently, the upturn of the $\Delta\nu / \nu^{\text{iso-high } T}$ ratio seen for DMP (Fig. 6c) is not due to a thermodynamic singularity (phase transition) but should be of *kinetic* origin. In fact, DMP crystallizes at 2 °C, and no effect of this thermodynamic transition is expected at much higher temperatures (≥ 14 °C) examined in Fig. 6. Thus, the upturn emerging at 36 °C and growing on a decrease of T (down to 14 °C) may be due to a multiple-activation mechanism of flow (due to a distribution of the activation energy E_a for flow). An additional possibility is a shrinkage of a “free volume” on cooling not fully incorporated in the Eyring model, as frequently argued for polymeric liquids^{2, 18}: This shrinkage changes the T dependence of ν from the Eyring/Andrade-type (eq 8) to the WLF-type^{2, 18}, which could have resulted in an upturn of the $\Delta\nu / \nu^{\text{iso-high } T}$ ratio observed for DMP.

Table II Parameters for asymptotic $\nu^{\text{iso-high } T}(T)$.

system	$10^{10} \nu^\infty / \text{m}^2 \text{s}^{-1}$	$E_a / \text{kJ mol}^{-1}$
pure 5CB	1.38	31.0
pure DMP	2.44	26.4
DMP/5CB mixture	0.85	32.2

Fig. 6 Temperature dependence of normalized deviation of the kinematic viscosity, $\Delta v/v^{\text{iso-high } T}$ with $\Delta v = v - v^{\text{iso-high } T}$, observed for pure 5CB, pure DMP, and DMP/5CB mixture. Black double-headed arrow highlights a discontinuous jump of $\Delta v/v^{\text{iso-high } T}$ of pure 5CB at T_{IN} . The sense of the symbols is the same as in Fig. 2.

For the pure 5CB system in the isotropic 1-phase state, the upturn of $\Delta v/v^{\text{iso-high } T}$ seen in Fig. 6a might be partly contributed from a similar kinetic effect(s). However, the deviation emerges only in a close vicinity of T_{IN} (within 3 K; see unfilled green squares), so that it should be dominantly contributed from the thermodynamic NI transition. The upturn noted for the DMP/5CB mixture in the isotropic 1-phase state should be also related to the NI transition (associated with the phase separation), because 5CB is the dominant component in the mixture ($w_{\text{5CB}} = 96.9 \text{ wt\%}$) and also because the deviation emerges for the mixture at $\sim 40^\circ\text{C}$ (cf. Fig. 6b) where the pure DMP system still follows the high- T asymptote.

As discussed above, the upturn of $\Delta v/v^{\text{iso-high } T}$ (*i.e.*, an extra enhancement of the viscosity compared to the high- T asymptote) seen for the 5CB and DMP/5CB systems should commonly have the thermodynamic origin related to the NI transition. Nevertheless, we note a difference between these systems: Fig. 6 demonstrates that the upturn occurs only in a close vicinity of T_{IN} (within 3 K) for pure 5CB but in a much wider range of T (between T_{IN}^* and $T_{\text{IN}}^* + 13\text{K}$) for the DMP/5CB mixture. This difference can be related to a difference in the fluctuation underlying the enhancement of the viscosity. Namely, the viscosity is enhanced when the inter-particle (inter-molecular) force reaches a longer distance

to correlate more molecules, as discussed for eq 7.

In the pure 5CB system, this correlation is related to the bulk compressibility κ_G governing the density fluctuation in this system. κ_G is usually very small so that the correlation emerges just for neighboring molecules and accordingly the density fluctuation remains short-ranged, unless in the close vicinity T_{IN}^* where κ_G increases significantly. This mechanism results in the enhancement of viscosity of the pure 5CB system (in the isotropic 1-phase state) just in the close vicinity of T_{IN} . In contrast, in the DMP/5CB mixture, the osmotic compressibility κ_{II} plays a key role. Even at T well above T_{IN}^* , κ_{II} is much larger than κ_G thereby allowing molecules in the mixture separated far away to be softly correlated (through the osmotic interaction) to exhibit a long-ranged concentration fluctuation (in addition to the short-ranged density correlation governed by the small κ_G). κ_{II} increases on cooling in a wide range of T down to T_{IN}^* (as can be noted from the concentration fluctuation being enhanced in that range of T), which results in the gradual enhancement of the viscosity of the mixture in the wide range of T , as observed in Fig. 6b.

Finally, a comment needs to be added for the positive deviation from the simple thermal expansion, *i.e.*, an extra densification, observed for the density of both 5CB and DMP/5CB systems (Fig. 3). This extra densification is related to κ_G in the pure 5CB system and to both κ_G and κ_{II} in the DMP/5CB mixture, and the above argument for the increase of κ_G and κ_{II} on cooling suggests that the extra densification occurs only in the close vicinity of T_{IN} for pure 5CB but in a wider range of T for the DMP/5CB mixture. At the same time, we also note that the range of T where the extra densification occurs is a little narrower than that for the extra enhancement of the viscosity; these densification and viscosity enhancement are observed within 1K and 3K above T_{IN} for pure 5CB, and within 10K and 13K above T_{IN}^* for the DMP/5CB mixture. This delicate difference might reflect a difference in the effect of fluctuation on the thermodynamic and kinetic quantities (density and viscosity). This difference in the fluctuation effect deserves further attention.

4. CONCLUDING REMARKS

In this study, we have examined the mass density ρ and zero-shear viscosity η of a DMP/5CB mixture ($w_{\text{DMP}} = 3.1 \text{ wt\%}$) and discussed a difference between this mixture and pure 5CB. Pure 5CB exhibited discontinuous jumps of ρ and η at the isotropic-to-nematic (IN) transition temperature $T_{\text{IN}} (\cong 35.0^\circ\text{C})$ whereas the DMP/5CB mixture showed no discontinuity at its $T_{\text{IN}}^* (\cong 27.0^\circ\text{C})$. This lack of

discontinuity for the mixture resulted from the phase separation into the isotropic and nematic phases occurring at T_{IN}^* , and cannot be regarded as an essential difference from the pure 5CB system. (The discontinuous jumps would have occurred for ρ and η of the nematic phase in the mixture but was smeared for the mixture as a whole, because of a continuous change of the volume fraction of that phase with T .)

Nevertheless, a characteristic difference was found between the DMP/5CB mixture and pure 5CB in the 1-phase isotropic state at $T > T_{IN}^*$ and/or T_{IN} . Both systems showed simple thermal expansion of the specific volume v_{sp} ($= 1/\rho$) and the simple Eyring/Andrade-type T dependence of the kinematic viscosity $\nu = \eta/\rho$ at sufficiently high T , and exhibited positive deviation from these high- T asymptotes on a decrease of T toward respective IN transition temperatures. However, the deviation was observed only in a close vicinity of T_{IN} (within a few K) for the pure 5CB system but in a much wider range of T (over 10K or more) for the DMP/5CB mixture. This difference between the two systems is related to an increase of the osmotic compressibility κ_{II} in the mixture in a wide range of T above T_{IN}^* (as reflected in enhanced concentration fluctuation at those T). The behavior of pure 5CB in the vicinity of T_{IN} is governed by the bulk compressibility κ_G ($\ll \kappa_{II}$), not by κ_{II} , which results in the difference between the two systems.

Thus, the current study suggests an importance of the osmotic effect (molecular correlation reflected in the concentration fluctuation) in the behavior of the DMP/5CB mixture in the 1-phase isotropic state. It is very interesting to experimentally detect this fluctuation (through dynamic scattering experiments, for example) and quantify the osmotic effect on the density and viscosity. It is also interesting to examine the osmotic effect on the dynamics of individual molecules (detected with dielectric experiments, for example). These experiments and related analysis are considered as an important subject of future study.

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