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Re-investigation of translational-orientational coupling behavior of nematogen in isotropic phase with non-nematogenic additives
等方相における液晶-非液晶混合系の並進配向結合挙動の再検討

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1. Introduction

Investgations on the translational orientation coupling constant *R* had been extensively carried out on various liquids by many research groups by observing the Rytov dip in GHz range using depolarized light scattering method with Fabri-Perot interferometer before 1980 [1]. The values of *R* depend on kind of molecular species but were almost indendent of termperature.

Matsuoka *et al*. developed a high resolution dynamic light scattering method based on heterodyne techinque and observed the Rytov dip in the MHz range on a nematogen (4-cyano-4’-hexylbiphenyl , 6CB) in the isotropic phase[2]. Shibata *et al*.[3] and Hirano *et al*.[4] found that the values of *R* decreases near the pseudo critical temperature *T** in nematogens in the isotropic phase and discussed temparature dependence of *R*.

Shibata *et al*.[5,6] investigated effects of non-nematogenic addtives on *R*. They reported that the value of *R* decreased with increasing molar fraction, and the decreasing ratio was at least 70% with addtives of mole fraction 0.10 in the temperature range of 15 K above *T**. In our preliminary unpublished results using high frequency strain optical coeffiecient measurements, although the value of *R* decreases with the addition of the mixture, the decreasing ratio of *R* is at most 30% with addtives at mole fraction 0.10. Results are not consistent each other and this inconsistency should be resolved.

Aim of this study is to re-investigate the effect of non-nematogenic additives on *R* using improved heterodyne dynamic light scattering and frequency dependent shear viscosity measurements.

2. Experimental

Heterodyne dynamic light scattering method was that used in the literatures [2-6]. To reduce the harmful electric noise and the effect from concentration fluctuation in the mixtures at low frequency, we adopted the acousto-optic frequency shifter. To reduce data scattering, the number of averaging procedure was adjusted considering the standard deviation of acquired data during measurements. Frequency spectra were measured on the logarithmic axis because translational-orientaional coupling effect on VH scattering spectra appears in low frequency region.

Frequency dependence of shear viscosity were also measured with shear impedance spectrometer in the frequency range of 5-205 MHz, which was described in detail in the literature[8].

Nematogen sample 4-cyano-4’-pentylbiphenyl (5CB) was supplied from Kanto Chemical Co. Inc. Non-nematogenic additives, carbon tetrachloride (CCl_4) was supplied from Wako Pure Chemical Industries, Ltd., and triphenyl phosphite (TPP) was supplied from Sigma-Aldrich. Samples 5CB and TPP were used after drying over 12 hours in the vacuum drying oven at 60 °C.

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3.Results and discussion

Figure 1 shows the VH scattering spectrum of the 5CB with addition of CCl_4 at mole fraction 0.10 by the heterodyne dynamic light scattering method at about 15 K above *T**. Note that the spectrum has a peak around 1 MHz and that the decrease of intensity with decreasing frequency below 1 MHz is clearly observed. This means that the value of *R* is not small. The solid curve indicates the fitting one with the theoretical equation below for VH

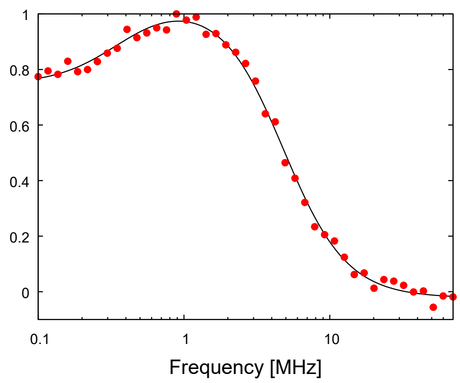

Fig. 1 VH scattering spectrrum of 5CB with addition of 0.1 mole CCl_4 at temperature above 15 K from the pseudo critical point.

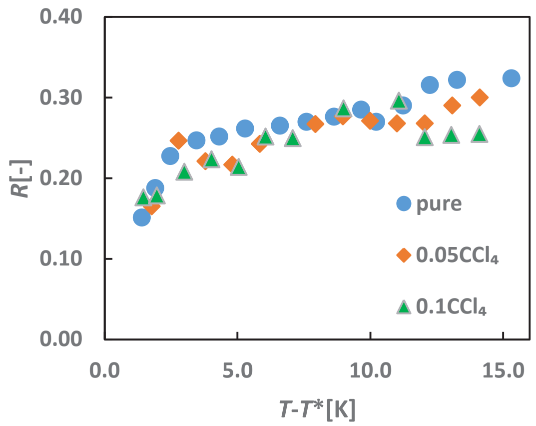

Fig. 2 Temperature dependence of R on 5CB-CCl_4 mixtures obtained by VH dynamic light scattering experiments

scattering:

$$I(f)=\frac{A\cdot f_r\left(f^2+f_{sh}{}^2(1-R)\right)}{(f^2-f_r\cdot f_{sh})^2+f^2\left(f_r+f_{sh}(1-R)\right)^2} \quad (1)$$

Here, I is scattering intensity, f is frequency, f_r is orientation relaxation frequency, and f_{sh} is defined as $f_{sh}=[(\eta/\rho)q^2]/(2\pi)$. Here η, ρ, q are the shear viscosity, the density and the wavenumber, respectively. A is a proportionality constant. The values of f_r, η, ρ, and q are determined by the VV scattering measurement, by the viscometer, by the vibrating-tube densitometer, and by calculation from scattering angle and the laser wavelength, respectively. Thus, fitting parameters are A and R.

Figure 2 shows $T-T^*$ dependence of R in pure 5CB and 5CB-CCl_4, mixtures, where T is the temperature. No distinct differences are observed even with addition of 0.10 mole CCl_4.

Figure 3 shows reduced relaxation spectra of shear viscosity at $T-T^*\approx 15$ K in 5CB with addition of CCl_4 at 0.10 mole fraction. The real part shows the plateau around 100 MHz. Reduction ratio of the reduced viscosity at the plateau value corresponds to R. Theoretical equation of frequency dependence of shear viscosity in which translational-orientational coupling is considered is given by

$$\eta^*/\eta_0=1-R\frac{if}{if+f_r} \quad (2)$$

Here, $\eta^*=\eta'-i\eta''$ is complex shear viscosity, and η_0 is the zero-frequency viscosity. Solid curves in Fig. 3 are the fitting curves with fitting parameter R.

The values of R in 5CB-CCl_4 mixtures at $T-T^*\approx 15$K are summarized in **Table 1**. The values of R in this study do not show significant decrease in contrast to those in our previous study [5].

Results in 5CB-TPP mixtures are the almost the same as those obtained in 5CB-CCl_4 mixtures. Significant decrease in R in mixtures in our

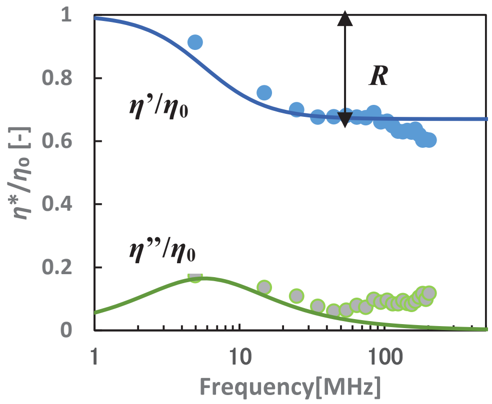

Fig. 3 Frequency dependence of reduced shear viscosity of 5CB with addition of 0.1 mole CCl_4 at temperature above 15 K from the pseudo critical point.

Table 1. The values of R in 5CB-CCl_4 mixtures at $T-T^*\approx 15$K in the previous study[5] and in this study.

mole fraction of CCl_4	VH dynamic light scattering [a]	VH dynamic light scattering	Frequency dependence of shear viscosity
0	0.30	0.32	0.35
0.05	0.20	0.30	0.35
0.10	0.09	0.25	0.32

a Ref. 5

previous studies [5,6] comes from insufficient preparation of light scattering equipment.

In this study, we re-investigated the effect of non-nematogenic additives on R using VH heterodyne dynamic light scattering and frequency dependent shear viscosity measurements on 5CB-CCl_4 and 5CB-TPP mixtures. The values of R did not show significant decrease with addition non-nematogenic compounds in the concentration investigated in this study.

References

1. G. R. Alms, T. D. Gierke and G. D. Patterson: J. Chem. Phys. **67** (1977) 5779 and references therein.
2 T. Matsuoka, K. Sakai and K. Takagi: Phys. Rev. Lett. **71** (1993) 1510.
3.T. Shibata, T. Matsuoka, S. Koda and H. Nomura: J. Chem. Phys. **109** (1998) 2038.
4. T. Hirano, T. Takagi and K. Sakai: Phys. Rev. E **72** (2005) 041407.
5. T. Shibata, T. Matsuoka, S. Koda and H. Nomura: Jpn. J. Appl. Phys. **38** (1999) 2059.
6. T. Shibata, T. Matsuoka, S. Koda and H. Nomura: J. Mol. liq. **85** (2000) 219.
7. T. Yamaguchi, S. Miyake and S. Koda: J. Phys. Chem. B **114** (2010) 8126.