Decoupling between the Temperature-Dependent Structural Relaxation and Shear Viscosity of Concentrated Lithium Electrolyte

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Abstract

The intermediate scattering functions of concentrated solutions of $LiPF_6$ in propylene carbonate (PC) were measured at various temperatures, two different wavenumbers, and three different concentrations using neutron spin echo (NSE) spectroscopy. The temperature dependence of the relaxation time was larger than that of the steady-state shear viscosity in all the cases. The shear relaxation spectra were also determined at different temperatures. The normalized spectra reduced to a master curve when the frequency was multiplied by the steady-state shear viscosity, indicating that the temperature dependence of the steady-state shear viscosity can be explained by that of the relaxation time of the shear stress. It is thus suggested that the dynamics of the shear stress is decoupled from the structural dynamics at the molecular scale.

1. Introduction

Shear viscosity is a transport property of liquids that governs macroscopic flows. In addition, microscopic dynamic processes in liquids have also been related to the shear viscosity. It is thus of both practical and academic importance to understand the microscopic mechanisms that determine the shear viscosity.

According to the Kubo-Green theory, the steady-state shear viscosity is given by the time-integral of the time correlation function of the shear stress.[1,2] It is thus approximately proportional to the relaxation time of the fluctuation of the shear stress, and an important question which remains is what are the microscopic modes that are coupled to the shear stress.

One of the important candidates is the density mode at the wavenumber of the main peak of the static structure factor. The structure factor of simple liquids shows a peak at the wavenumber that corresponds to the reciprocal of the intermolecular contact distance, which is called "main peak" in this work.[1] The relaxation of the intermediate scattering function is slow at the main peak, which is well-known as the de Gennes narrowing. The mode-coupling theory (MCT) predicts that the slow dynamics of simple viscous liquids, including the shear relaxation, is governed by the structural relaxation at the main peak.[3]

The relaxations of the isotropic and the anisotropic parts of the stress tensor, which are related to the bulk and the shear viscosity, respectively, have been studied on various viscous liquids using ultrasonic techniques.[4] They have been traditionally called “structural relaxation” under the consideration that they originate from the relaxation of microscopic density modes. However, the actual relation between the relaxations of the stress tensor and the density mode is still an open question.

The intermediate scattering function can be measured experimentally using quasi-elastic scattering techniques such as neutron spin-echo (NSE) spectroscopy.[5,6,7,8,9,10,11,12] The structural relaxation of some viscous liquids was actually determined at the main peak, and the temperature dependence of the relaxation time was usually compared with that of the steady-state shear viscosity. Both quantities were proportional to each other in most cases, while Pravel and coworkers reported the stronger temperature

dependence of the structural relaxation time than that of the steady-state shear viscosity in the case of a concentrated solution of LiCl in D_2O.[11~~10~~]

The relationship between the structural relaxation time and the steady-state shear viscosity has also been a target of computational works on supercooled liquids. Some studies reported that the temperature dependence of the steady-state shear viscosity was stronger than that of the relaxation time of the intermediate scattering function at the main peak, although the self-part of the intermediate scattering function was used in these studies instead of the collective part.[13,14]

We have reported the intermediate scattering functions of a concentrated lithium electrolyte, the solution of $LiPF_6$ in propylene carbonate (PC), at 298 K and various concentrations, which were determined experimentally using NSE spectroscopy.[15] The results were compared with the frequency-dependent shear viscosity, and it was suggested that the shear relaxation was governed by the structural dynamics at the main peak. In this work, we present the temperature dependence of the structural relaxation time, which is also compared with that of the steady-state shear viscosity. The temperature dependence of the shear relaxation spectra was also measured in order to examine the relationship between the steady-state shear viscosity and the shear relaxation time.

PC is a representative model solvent for a lithium ion battery, and the shear viscosity of the lithium ion electrolyte is a physicochemical quantity that is correlated with the ionic mobility.[16,17] The temperature dependence of the electrolyte is thus of practical importance for the use of the battery under cold condition. In addition to the results on the solution of the lithium salt, we present the structural dynamics of neat PC, which is a typical example of molecular supercooled liquids. Its dynamics has been studied in various ways[18] such as dielectric spectroscopy,[19,20] Brillouin scattering[21] and diffusion measurement.[22] We thus consider that the insights obtained by our present work is not limited to electrolyte solutions, but extend to the dynamics of supercooled liquids in general.

2. Experimental[§]

The materials and the methods for the NSE measurement were described in detail in our previous paper.[15~~14~~] Briefly, $LiPF_6$ (Kishida Chemical) was dissolved into PC-d_6 (CDN Isotope) with the concentrations of 0 (neat PC), 1 mol/kg, 2 mol/kg and 3 mol/kg. These samples were mixed and loaded in Al cylindrical sample cell with a sample thickness of 1 mm in a He atmosphere with a moisture control. The sample temperature was controlled using a top-loading closed cycle refrigerator with a temperature accuracy within ±1 K at the NGA-NSE beam line at the NIST Center for Neutron Research.[23] Using incoming neutron wavelength, λ, of 0.5 nm with a wavelength distribution of about 20%, we measured normalized intermediate scattering function, $I(Q,t)/I(Q,0)$, from the samples at Q = 10 nm^{-1} and 14 nm^{-1} in the Fourier time, t, range from 5 ps to 10 ns, where Q denotes momentum transfer, $Q = 4\pi\sin(\theta/2)/\lambda$ with θ the scattering angle. The sample scattering at a base temperature (10 K) was used as a resolution function for the instrument. The DAVE software was used to correct for the instrumental resolution and to obtain $I(Q,t)/I(Q,0)$.[24] Error bars represent ±1 standard deviation throughout the paper.

The protonated solvent, PC-h_6, was used for the measurements of the steady-state shear viscosity and the shear relaxation spectra. The temperature dependence of the density and the steady-state shear viscosity was measured using two different Stabinger-type viscometers, namely, SVM3000G2 (Anton Paar) at CRIEPI and SVM3001 (Anton Paar) at Nagoya University. The former was used for the solutions of 1 mol/kg, 2 mol/kg, and 3 mol/kg at the temperatures between 283 K and 353 K. The latter was applied to neat PC in addition to the three concentrations noted above. The temperatures of the measurement were below 303 K for solutions and below 313 K for the neat solvent. The agreement of

[§] Certain trade names and company products are identified in order to specify adequately the experimental procedure. In no case does such identification imply our recommendation or endorsement, nor does it imply that the products are necessarily the best for the purpose.

the values determined by the two facilities was within 5 % in the overlapping temperature region. The validity of the measured viscosity of neat PC was confirmed by the agreement with the values reported in the literature.[25,26]

We would like to comment here on the H/D substitution effect on the shear viscosity of PC. It is well-known that the H/D substitution modifies both equilibrium and dynamic properties of liquid water,[27] and the isotopic effects are ascribed to the strengthening of the hydrogen-bonding upon deuteration. In the case of PC, however, all the hydrogen atoms substituted are C-H protons which do not form hydrogen bond. In the case of liquid benzene, for example, the increase in the shear viscosity upon deuteration is several percent, which is approximately explained by the increase in the total mass.[28] We thus consider that the variation of the shear viscosity upon the deuteration of PC is marginal to affect the discussion in this work.

The shear relaxation spectra of the solutions were measured at 2 mol/kg and 3 mol/kg. The temperatures of the measurements were 298 K, 280 K, 260 K and 250 K for 2 mol/kg solution, while 320 K, 310 K, 298 K, 290 K, 280 K and 270 K for 3 mol/kg solution. The experimental methods and devices were described in detail in the literature.[29,30,31] The frequency range was between 5 MHz and 205 MHz. The temperature of the sample was controlled by flowing water through the sample cell at the temperatures above 273 K. The stability of the temperature was within ± 0.2 K. Silicone oil was used as a thermostat fluid instead of water below 273 K, and the temperature stability was within ± 0.5 K. The standard errors in the complex shear relaxation spectra, $\eta(\nu)$, were $|\delta\eta(\nu)/\eta_0| < 0.1$ in the frequency region between 15 MHz and 95 MHz, and $|\delta\eta(\nu)/\eta_0| < 0.2$ at other frequencies, where η_0 stands for the steady-state shear viscosity.

3. Results and Discussion

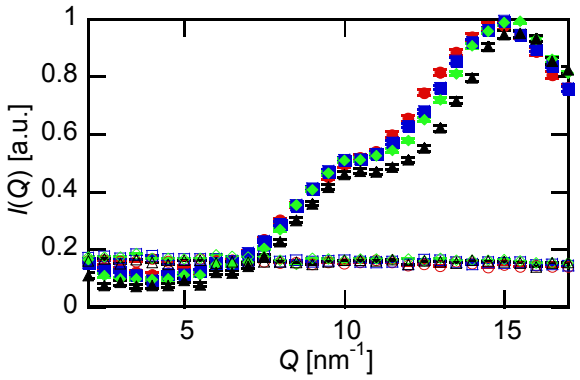

Figure 1. Neutron diffraction patterns of 3 mol/kg solution of $LiPF_6$/PC measured on the NSE spectrometer are plotted as a function of wavenumber, Q. The temperatures of the measurements were 320 K (red), 298 K (blue), 270 K (green), and 240 K (black). The coherent and incoherent parts are shown with filled and open symbols, respectively. The result at 298 K was the same as that shown in Ref. 15~~14~~.

Figure 1 shows the static structure factor of 3 mol/kg solution at various temperatures, which were determined using the NSE spectrometer. The results at other concentrations, including 0 mol/kg (neat solvent), are shown in Figs. S1a to S1c of Supporting Information. The variation of the structure factor is small particularly between 270 K and 320 K. A weak temperature dependence was observed also for the other concentrations.

The coherent structure factors exhibit a small shoulder at 10 nm^{-1}, which is hereafter called "prepeak", in addition to the main peak at 14 nm^{-1}. The height of the prepeak decreases with decreasing the concentration, as is shown in Figs. 1 and S1a to S1c. Very recently, some of us revealed with the neutron diffraction with isotope substitution and molecular dynamics simulation techniques that the prepeak originates in the domain structure composed of the ionic and the nonpolar parts,[32] as in the case of ionic liquids with long alkyl chains.[33,34,35,36,37] The intermediate scattering functions were measured at Q = 10 nm^{-1} and 14 nm^{-1}, which correspond to the prepeak and the main peak, respectively.

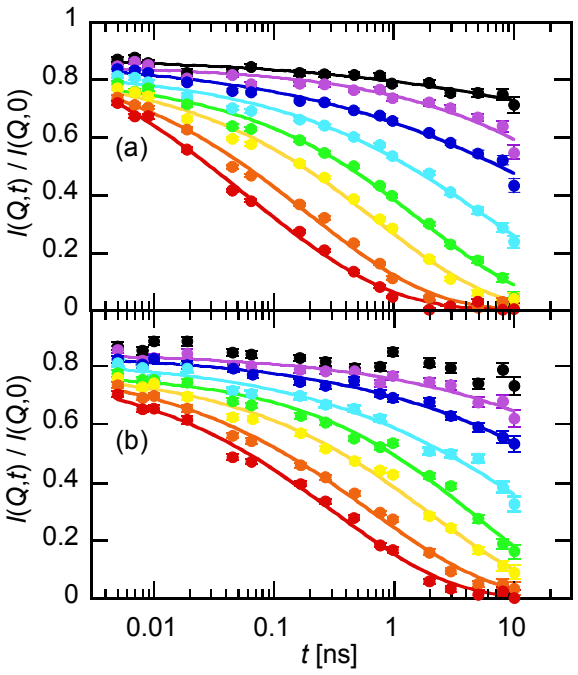

Figure 2. Intermediate scattering functions of 3 mol/kg solution of $LiPF_6$/PC at (a) Q = 14 nm^{-1} and (b) Q = 10 nm^{-1}. The temperatures of the measurements were 320 K (red), 310 K (orange), 298 K (yellow), 290 K (green), 280 K (aqua), 270 K (blue), 260 K (purple), and 250 K (black). The experimental data are shown with filled circles with error bars, while the fitting lines of the KWW function, eq. 1, are shown with solid curves.

The normalized intermediate scattering functions at Q = 14 nm^{-1} (main peak) and Q = 10 nm^{-1} (prepeak) are shown in Figs. 2a and 2b, respectively, for 3 mol/kg solution, and those at other concentrations are in Figs. S2a to S4b of Supporting Information. The results at 298 K are the same as those in Ref. 15~~14~~. The relaxation of the intermediate scattering function becomes slower with decreasing temperature at all the concentrations as is expected. At the same temperature, the relaxation becomes slower with increasing the concentration of the salt, which is in harmony with the increase in steady-state shear viscosity. The relaxation at the prepeak is slower than that at the main peak except for the neat solvent, which exhibits no prepeak structure.

The intermediate scattering functions at two wavenumbers were approximated by the Kohlrausch-Williams-Watts (KWW) function as

$$\frac{I(Q,t)}{I(Q,0)} = A\exp\left[-\left(\frac{t}{\tau}\right)^{\beta}\right]. \quad (1)$$

All the three parameters, A, τ, and β, were treated as free adjustable parameters except for $I(Q,t)$ of the neat solvent at Q = 10 nm^{-1}, where only the slowest tail of the intermediate scattering function was accessible by our NSE experiment as is shown in Fig. S4b. The value of A was fixed to be 0.85 for $I(Q,t)$ of neat PC at Q = 10 nm^{-1}, which is a typical value at other conditions as will be shown later, and the other two parameters, β and τ, were optimized.

The parameters A and β, which represent the amplitude and the distribution of the relaxation times, respectively, are plotted in Figs. S5 and S6 of Supporting Information as the function of temperature. The amplitude A lies around 0.8 to 0.9 at all the temperatures and concentrations, except for higher temperature regions where the relaxation of the intermediate scattering function is fast and the initial part of the relaxation function was not observed within the time window of our NSE experiment. The error in A under such conditions is large, and β also suffers large errors there. We thus consider that the time window was not sufficient under these conditions to determine the three parameters simultaneously. The values of β scatters around 0.5, except for those of 1 mol/kg solution at Q = 10 nm^{-1}. Since the height of the prepeak is low at 1 mol/kg, the scattering at Q = 10 nm^{-1} originates both from the prepeak and the low-Q edge of the main peak. We consider that the apparent large distribution of the relaxation time (small β) there is to be ascribed to the overlap of these two contributions.

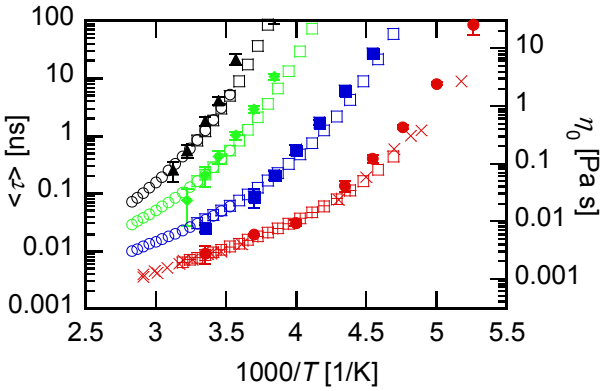

Figure 3. The mean relaxation time of the intermediate scattering function at Q = 14 nm^{-1}, $<\tau>$ (left axis), and the steady-state shear viscosity, η_0 (right axis), are plotted against the reciprocal temperature. The concentrations of the salt are 0 (red), 1 mol/kg (blue), 2 mol/kg (green), and 3 mol/kg (black), respectively. The mean relaxation times are plotted with filled symbols. The steady-state shear viscosity measured at CRIEPI and Nagoya University is shown with open circles and open squares, respectively. The steady-state shear viscosity values of neat PC reported in Refs. 25~~19~~ and 26~~20~~ are plotted with + and ×, respectively.

The mean relaxation time of the KWW function, $<\tau>$, is defined as

$$\langle \tau \rangle \equiv \frac{\tau}{\beta} \Gamma\left(\frac{1}{\beta}\right), \tag{2}$$

where $\Gamma(x)$ stands for the gamma function. The mean relaxation times of the intermediate scattering functions were evaluated from the KWW fitting parameters through eq. 2. The values of $<\tau>$ at Q = 14 nm^{-1} are plotted against the reciprocal temperature together with the steady-state shear viscosity, η_0.

At ambient temperature, $1000/T$ = 3.3 K^{-1}, the increase in $<\tau>$ with the salt concentration correlates with that in η_0. We have demonstrated in our previous work that the shear relaxation spectra of $LiPF_6$/PC solutions at 2 mol/kg and 3 mol/kg are explained by the respective intermediate scattering functions at the main peak using MCT. The correlation between $<\tau>$ and η_0 is thus quite natural, and it can be understood as that the structural relaxation at the main peak determines η_0 through the shear relaxation dynamics. Comparing the temperature dependences of $<\tau>$ and η_0, however, the slowing down of the former with decreasing the temperature is stronger than the increase in the latter at all the concentrations including the neat solvent.

There are two different ways to compare the temperature dependences of $<\tau>$ and η_0. The first one is to examine the proportionality between these two values as is performed in this work.[10] This comparison stems from the Maxwell model of viscoelasticity as

$$\eta_0 = G_\infty \tau_\eta , \quad (3)$$

where G_∞ and τ_η stand for the high-frequency limiting shear modulus and the shear relaxation time. Assumption of the temperature independence of the former yields the proportionality between η_0 and τ_η.

The second way of comparison is to expect the proportionality between τ and η_0 / T,[38] which is deduced based on the following ideas. The relaxation time of the density mode, τ, is reciprocally proportional to a kind of diffusion coefficient, denoted as D, which is in turn related to η_0 by the Stokes-Einstein relationship as $D \propto T / \eta_0$. The combination of $\tau \propto 1/D$ and $D \propto T / \eta_0$ yields the proportionality between τ and η_0 / T.

In this work, we mainly employed the first idea and compared directly the temperature dependence of $<\tau>$ and η_0. We also tried the comparison between τ and η_0 / T, and the results are essentially the same as will be shown later.

The intermediate scattering functions are plotted against the time divided by the steady-state shear viscosity, t / η_0, in Figs. S7a to S10b of Supporting Information in order to demonstrate the decoupling between η_0 and $<\tau>$ in a different way. The formation of a master curve is not recognized, and the relaxation becomes slower with decreasing temperature on the t / η_0 axis except for neat PC at Q = 10 nm^{-1}. It indicates that the temperature dependence of the relaxation time is stronger than that of the steady-state shear viscosity, and the decoupling between η_0 and $<\tau>$ is not an artifact caused by the KWW analysis.

The relaxation time of the neutron intermediate scattering function of neat PC-h_6 was reported by Börjesson and Howells as a function of temperature.[39] The self-motion is mainly probed by the neutron quasi-elastic scattering of protonated samples due to the large incoherent scattering length of protons. Comparing their relaxation time at Q = 16 nm^{-1} with ours at Q = 14 nm^{-1}, it should be noticed at first that the absolute value of the former is far smaller than the latter. The relaxation time of PC-d_6 is about 1 ns at 210 K ($1000/T$ = 4.8 K^{-1}), while that of PC-h_6 at the corresponding temperature is about 100 ps. In addition, the temperature dependence of the relaxation time of PC-h_6 is a little weaker than that of the

steady-state shear viscosity, which is opposite to our present results on neat PC-d_6. The different tendencies in PC-d_6 and PC-h_6 suggests the difference between the self- and the collective parts of the intermediate scattering function, although the larger value of Q in PC-h_6 experiments may be a reason of faster relaxation and the intramolecular dynamics of the methyl group may contribute to the incoherent intermediate scattering function of PC-h_6. The self-part of the intermediate scattering function is often used in computational studies for the evaluation of the structural relaxation time, mainly due to the relative ease for the calculation of the self-part. However, since the coupling between the shear stress and the collective density modes is considered in MCT, our present result underscores the importance of the numerical evaluation of the collective part.

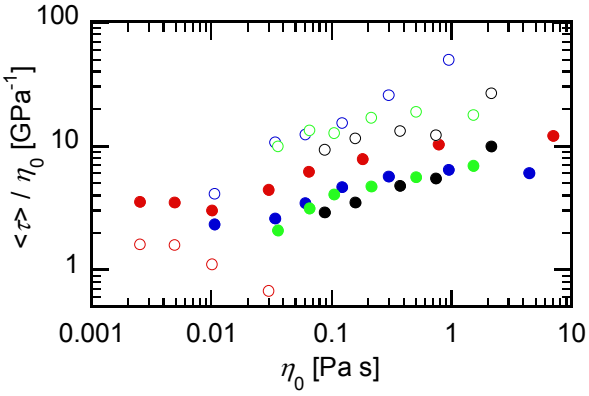

Figure 4. The mean relaxation times of the intermediate scattering function at the prepeak (Q = 10 nm^{-1}, open) and the main peak (Q = 14 nm^{-1}, filled) divided by the steady-state shear viscosity are plotted as the function of the steady-state shear viscosity. The concentrations of the salt are 0 (red), 1 mol/kg (blue), 2 mol/kg (green), and 3 mol/kg (black), respectively.

The mean relaxation times at both wavenumbers are divided by η_0 and plotted against η_0 in Fig. 4. The data points of $<\tau>$ > 100 ns were excluded from the plot because they involve large errors. The ratios of $<\tau>$ to η_0 are an increasing function of η_0 at both wavenumbers and all the concentrations except for that of neat PC at Q = 10 nm^{-1}. The magnitude of the increase depends little on the wavenumber and the salt concentrations. In short, the structural relaxation of neat PC and $LiPF_6$/PC

solutions is decoupled from the steady-state shear viscosity, and the former exhibits stronger temperature dependence than the latter.

The longitudinal axis of Fig. 4 is changed to $<\tau> T / \eta_0$ in Fig. S11 in order to test the proportionality between $<\tau>$ and η_0 / T. The ratio is still an increasing function of η_0, although the slope is a little smaller than that in Fig. 4. The decoupling between the structural relaxation time and the steady-state shear viscosity is thus evident in the comparison between $<\tau>$ and η_0 / T, as well.

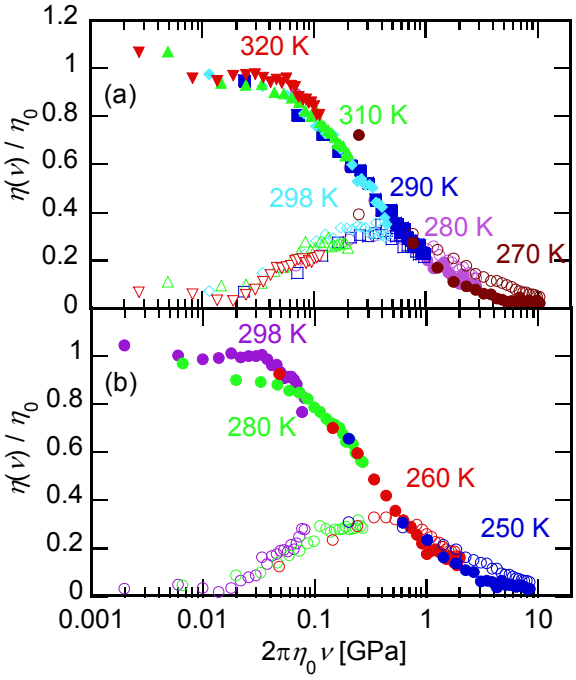

Figure 5. The normalized shear relaxation spectra, $\eta(\nu)/\eta_0$, are plotted against the frequency reduced to η_0. The concentrations of the salt are (a) 3 mol/kg and (b) 2 mol/kg, respectively. The real and imaginary parts are shown with the filled and the open symbols, respectively. The spectra at different temperatures are shown with different colors, and the correspondence between the temperatures and the colors are indicated within the panels.

The steady-state shear viscosity is approximately given by the product of the shear relaxation time and the high-frequency limiting shear modulus as is described in eq. 3. The coupling between the structural relaxation and the shear viscosity usually means that the shear relaxation time is proportional to the structural relaxation time, with a constant limiting shear modulus. The assumption of the constant

limiting shear modulus does not necessary hold, however, and we need to examine the temperature dependence of the shear relaxation time before discussing the decoupling between $<\tau>$ and η_0.

The shear relaxation time of viscous liquids can be probed through the measurement of the frequency-dependent complex shear viscosity, that is, shear relaxation spectrum. We measured in this work the shear relaxation spectra of the solutions of 2 mol/kg and 3 mol/kg at various temperatures in order to examine the temperature dependence of the limiting shear modulus.

The normalized shear relaxation spectra are shown as the function of the reduced frequency in Figs. 5a and 5b. The spectra at different temperatures reduce to a master curve at both concentrations when plotted against the frequency reduced to η_0, contrary to what seen with the intermediate scattering functions shown in Figs. S7a and S8a of Supporting Information. In addition, the master curves at the two concentrations resemble each other. From the peaks of the imaginary parts, the reduced relaxation frequency is about 0.3 GPa. Since the peak frequency of the imaginary part approximately satisfies $2\pi\nu\tau_\eta \sim 1$, the value of 0.3 GPa can be regarded as G_∞ according to eq. 3. The reduction to the master curve indicates that the shear relaxation time is proportional to the steady-state shear viscosity, implying small variations of the limiting shear modulus. The decoupling between $<\tau>$ and η_0 observed in Figs. 3 and 4 is thus regarded as that between the dynamics of the shear stress and the density modes at the molecular scale.

The relationship between the relaxation times of the intermediate scattering function at the main peak and the steady-state shear viscosity has been studied on some viscous liquids experimentally. The proportionality between the structural relaxation time and the steady-state shear viscosity was confirmed on representative supercooled liquids including glycerin and *o*-terphenyl.[54,65,76] The shear relaxation measurement by one of us recently demonstrated that the proportionality also holds between the relaxation times of the density mode and the shear stress.[40] On the other hand, the larger temperature dependence of the former than that of the latter, as is observed in our present work, was also reported on $LiCl/D_2O$ by Pravel and coworkers.[11,10] Some computational studies suggested a weaker temperature

dependence of the density mode relaxation,[13,14] although such a decoupling has not been observed experimentally to the best of our knowledge.

One may suspect that the stronger temperature dependence of the structural relaxation time may have something to do with the presence of ions, because it is common to both $LiPF_6$/PC and $LiCl/D_2O$ solutions. However, we have observed the same decoupling on neat PC without salts, and the degree of the decoupling is as large as that of the electrolyte solutions. In addition, the decoupling between the structural relaxation and the steady-state shear viscosity was not observed on ionic liquids, where the concentration of ions is quite high.[8]

The relationship between the structural relaxation and the shear viscosity has been studied as one of the universal properties of supercooled liquids that govern the slow dynamics near the glass-transition temperature. However, our present result suggests that the relationship might be rather specific to individual systems, and we consider that extensive studies would be necessary to understand the characteristics of the stress-structure decoupling in terms of microscopic structures and interactions.

4. Summary

The structural relaxations of $LiPF_6$/PC solutions were measured as functions of temperature at various concentrations using NSE spectroscopy. The temperature dependence of the structural relaxation time was stronger than that of the steady-state shear viscosity. The shear relaxation spectra indicate that the temperature dependence of the steady-state shear viscosity is explained by that of the shear relaxation time. It was thus revealed that the dynamics of the shear stress is decoupled from that of the density mode at the main peak of the static structure factor in the cases of $LiPF_6$/PC solutions and neat PC. Further experimental studies will be required to clarify the general relationship, if any, between the structural and shear relaxations.

Acknowledgments

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Supporting Information

The Supporting Information is available free of charge via the Internet at http://pubs.acs.org/.

The static diffraction patterns and the intermediate scattering functions of $LiPF_6$/PC solutions at 0 mol/kg (neat solvent), 1 mol/kg and 2 mol/kg, the temperature dependence of the KWW parameters A and β, the intermediate scattering functions plotted against the reduced time, and $<\tau> T / \eta_0$ as the function of η_0.

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