High-frequency shear viscosity and ionic mobility of solutions of polyethylene glycol in ionic liquids

Tsuyoshi Yamaguchi* and Takujiro Kikuzawa

Graduate School of Engineering, Nagoya University, Furo-cho B2-3 (611), Chikusa, Nagoya, Aichi 464-8603, Japan.

E-mail: yamaguchi.tsuyoshi@material.nagoya-u.ac.jp

The frequency-dependent complex shear viscosity of the solutions of polyethylene glycol (PEG) in various ionic liquids are measured in the frequency range of 5 - 205 MHz, and the ionic mobility of the corresponding solutions were also determined.　The plateau viscosity in the MHz regime increases on the addition of PEG, and the relaxation in the 100 MHz regime is retarded simultaneously.　The amount of the increase in the plateau viscosity correlates with that in the relaxation time, suggesting that the retardation of the relaxation is a reason for the increase in the plateau viscosity.　Although the increase in the plateau viscosity is far smaller than that in the zero-frequency viscosity, these two values are correlated with each other, which can be explained as the consequence of the strength of the same kind of the solute-solvent attractive interaction.　The decrease in the molar ionic conductivity also correlates with the increase in the plateau viscosity, suggesting that the plateau viscosity can be regarded as the local viscosity of ionic liquids related to the ion conduction.　Based on the correlation with the Kamlet-Taft α parameter, the hydrogen bond between the ionic liquid and the oxygen atoms of PEG is suggested to be a possible origin of the increase in the plateau viscosity.

1.   Introduction

Room-temperature ionic liquid, nowadays called simply as "ionic liquid", is liquid composed solely of ions whose melting temperature is nonetheless below 100 °C.   Owing to its peculiar properties such as high ionic conductivity, negligible vapour pressure at ambient conditions, high thermal and electrochemical stabilities, high solubility of both organic and inorganic compounds, and so on, it is now regarded as a novel liquid material for various applications including electrolyte for electrochemical devices, lubricant, and solvent for organic reaction and separation [1,2].

Ionic liquids are sometimes immobilized by the dissolution of polymers for practical applications such as electrolyte for electrochemical devices and separation membrane [3,4].   The molecular mobility of constituent ions or solutes is a crucial property for such applications.   The mobility of molecules in liquid solutions is often discussed in terms of shear viscosity based on the hydrodynamic Stokes-Einstein relation. Although the macroscopic viscosity of the whole solution of polymer in an ionic liquid can easily be measured using conventional viscometer, what is related to the molecular mobility is the local viscosity of the ionic liquid between polymeric chains.

In our previous work, we determined the frequency-dependent complex shear viscosity of polymer gel electrolyte solutions in the MHz regime using shear impedance spectroscopy [5].   The complex shear viscosity showed a plateau in the MHz regime, whose value was much smaller than macroscopic viscosity. The increase in the plateau viscosity with the dissolution of polymers was correlated well with the decrease in the ionic mobility, and it was concluded that the plateau viscosity can be regarded as the local viscosity of the electrolyte that is related to the ion conduction.

In this work, we apply the same methodology to solutions of polymer in ionic liquid to obtain information on the local viscosity of ionic liquids between polymer chains.   The polymer is fixed to polyethylene glycol (PEG), which is a representative polymer used in physicochemical studies of polymer / ionic liquid solutions [6,7,8,9].   Both cations and anions of ionic liquids are varied systematically, and the results are discussed in terms of intermolecular interaction between PEG and ions.

2.　　　Experiments

PEG was purchased from Nacalai Tesque and used without further purification.　The molecular weight (M_w) of the sample used mainly was 20000 (PEG20k), and the sample of $M_w = 6000$ (PEG6k) was also used for comparison.　Eight ionic liquids were used as solvents, namely, 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide ([bmim][TFSA], Kanto Chemical), [bmim] hexafluorophosphate ([bmim][PF$_6$], TCI), [bmim] tetrafluoroborate ([bmim][BF$_4$], TCI), 1-ethyl-3-methylimidazolium [TFSA] ([emim][TFSA], TCI), 1-methyl-3-octylimidazolium [TFSA] ([omim][TFSA], IoLiTec), 1-butyl-2,3-dimethylimidazolium [TFSA] ([bmmim][TFSA], TCI), 1-butyl-1-methylpyrrolidinium [TFSA] ([bmpy][TFSA], TCI), and 1-butylpyridinium [TFSA] ([bpy][TFSA], TCI).　The set of ionic liquids consists of three series.　The anion was varied with keeping the cation as [bmim] in the first one, [bmim][TFSA], [bmim][PF$_6$] and [bmim][BF$_4$].　The length of 1-alkyl-3-methylimidazolium cation was varied in the second one, [emim][TFSA], [bmim][TFSA] and [omim][TFSA].　The polar head group of the cation was varied in the third one, [bmim][TFSA], [bmmim][TFSA], [bmpy][TFSA] and [bpy][TFSA].

The fraction of PEG in the solutions was fixed to be 5 wt%.　Both PEG and ionic liquid were measured by weight and contained in a round flask.　The flask was then evacuated by a rotary pump, and heated to 100 °C in an oil bath.　The mixture of the ionic liquid and PEG melt was then stirred under vacuum with a magnetic stirrer for more than 12 hours to remove residual water prior to measurements.　The water contents of some samples including [bmim][PF$_6$] solution of PEG20k were determined with a Karl Fischer Coulometer (Metrohm, 831KF), and the obtained values were below 300 ppm.　All the measurements were performed at 25 °C.

The frequency-dependent complex shear viscosity was measured by means of shear impedance spectroscopy [10, 11], whose experimental details were described elsewhere [12, 13].　Briefly, the resonance of AT-cut quartz crystal transducer was measured electrically before and after the contact with

sample solution, and the frequency-dependent complex viscosity was obtained from the changes in the resonance frequency and the bandwidth. The frequency range of the measurement was from 5 MHz to 205 MHz. The zero-frequency shear viscosity was measured using a commercial cone-plate viscometer (Brookfield, RV DV-I Prime with a spindle CPA-40Z). The apparent viscosity of all the samples including polymer solutions was independent of the shear rate within the range of our measurement, and we regarded the obtained value as the Newtonian viscosity.

The alternating-current (AC) conductivity was measured by means of impedance measurement using vector network analyser (Rhode & Schwarz, ZVL3/03) [14,15]. The sample liquid was contained in a parallel-plate cell, and the conductivity of the sample was obtained from the impedance between the electrodes. The impedance of the cell including a connector was approximated as an equivalent circuit, and the parameters of the circuit were determined based on the measurement of the reference samples of air and water. The diameter of the circular electrode was 4 mm, and the gap between two electrodes was about 0.3 mm. A Teflon fringe was attached to the circular electrode in order to keep the effects of the edge constant.

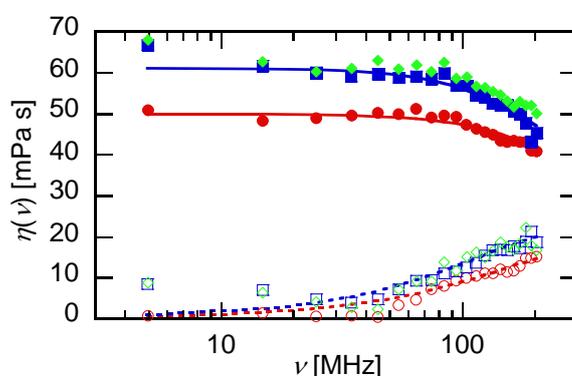3.   Results and Discussion

Figure 1.   The frequency-dependent complex shear viscosities of neat [bmim][TFSA] (red) and the solutions of PEG20k (blue) and PEG6k (green) in [bmim][TFSA]. The real and the imaginary parts

are plotted with filled and open symbols, respectively.   The real and the imaginary parts of the fitting curves using the Cole-Davidson function (eq. 1) are also shown with the solid and the dotted curves, respectively.

Figure 1 exhibits the frequency-dependent complex shear viscosity of [bmim][TFSA].   A relaxation is observed in the 100 MHz region in neat liquid.   The value of the real part is almost independent of frequency below 50 MHz, and it is close to the zero-frequency value determined with the conventional viscometer, 50.7 mPa s.   It can thus be said that there is no relaxation below 10 MHz, and the relaxation in the 100 MHz region is the slowest one that governs the zero-frequency viscosity [16].   Our recent theoretical and computational works demonstrated that the relaxation in the 100 MHz region is assigned mainly to the structural relaxation of the charge-density mode [17,18].

The relaxation in the 100 MHz region is also observed in polymer solutions.   In addition, both the real and the imaginary parts increase with decreasing frequency below 20 MHz.   Considering that the values of the zero-frequency viscosity, 273 mPa s and 141 mPa s for the solutions of PEG20k and PEG6k, respectively, are much larger than the corresponding values of the complex viscosity in the MHz region, there must be some relaxations below 1 MHz, and the frequency dependence of the complex viscosity below 20 MHz is regarded as the high-frequency edge of the relaxation below 1 MHz.   The difference between the zero-frequency viscosity and the complex viscosity in the MHz regime was also reported on polymer gel electrolytes [5].   The relaxation below 1 MHz was assigned to the relaxation of the modes of polymers, and we consider that the same assignment applies also to polymer / ionic liquid systems.

The plateau value of the complex viscosity of polymer solutions around 50 MHz is regarded as the viscosity of the solvent ionic liquid.   Figure 1 shows that the plateau viscosity of the polymer solutions is a little higher than the corresponding value of the neat ionic liquid.   In addition, the variation of the real part relative to the plateau value is stronger for the polymer solutions than for the neat liquid.   It suggests that the relaxation in the 100 MHz region is retarded by the dissolution of PEG, although quantitative analysis is required to show the degree of the retardation.   Since the relaxation in the 100 MHz region is assigned to the structural relaxation of the charge-density mode that governs the viscosity of ionic liquid,

its retardation is consistent with the increase in the plateau viscosity. The relaxation frequency of the solvent is higher than the experimental frequency range in our previous study on polymer gel electrolyte, and it is the first demonstration of the effect of polymer dissolution on the shear relaxation of solvent to the best of our knowledge.

In spite that the zero-frequency shear viscosity strongly depends on the molecular weight, the frequency-dependent complex shear viscosity of the polymer solutions is little dependent on M_w, which is natural considering that the viscosity of the solvent ionic liquid reflects the local interaction between the polymer chain and ions. Although the effect of the terminal groups increases with decreasing molecular weight, it seems rather small in the present system. The high-frequency edge of the polymer mode observed below 20 MHz is also independent of the molecular weight. Some ultrasonic relaxation studies on polymer solutions demonstrated that a relaxation mode independent of the molecular weight exists on the high-frequency side of the normal modes of the polymer, and the M_w-independent mode was assigned to the segmental motion [19,20]. We consider that the independence of the complex viscosity of polymer solutions below 20 MHz on the molecular weight is in harmony with the existence of the segmental mode in ultrasonic relaxation.
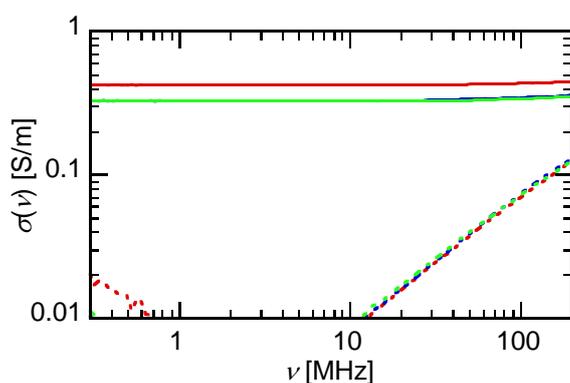

Figure 2. The AC conductivity of neat [bmim][TFSA] (red) and the solutions of PEG20k (blue) and PEG6k (green) in [bmim][TFSA]. The real and the imaginary parts are plotted with solid and dotted curves, respectively. The blue curves are almost indistinguishable because they are overlapped with the corresponding green ones.

The AC conductivity of the same solutions is exhibited in Fig. 2. The real part of the conductivity

shows a plateau value between 1–10 MHz, and the frequency dependence is found on both high- and low-frequency sides. The corresponding frequency dependence is also found in the imaginary part. The relaxation on the high-frequency side is assigned to the structural relaxation which is common to the complex shear viscosity. The frequency dependence on the low-frequency side is the apparent relaxation due to the polarization of the interface of the electrodes, and the plateau value in the MHz region is regarded as the direct current (DC) conductivity.

The DC conductivity decreases with the dissolution of PEG, which is partly ascribed to the decrease in the molar concentration of ions due to the excluded volume of PEG. As will be shown later, however, the decrease in the DC conductivity is stronger than that in the molar concentration, which is in harmony with the increase in the plateau viscosity demonstrated in Fig. 1.

The AC conductivity of polymer solutions is little dependent on the molecular weight, as is the case of the frequency-dependent complex shear viscosity in Fig. 1. It suggests that the decrease in the ionic mobility in polymer solutions is also determined by local interactions. The negligible dependence of both spectra on molecular weight is also confirmed on [bmim][PF$_6$] solutions, and we shall hereafter show the results on PEG20k solutions to examine the effects of the variation of ionic species.

The frequency-dependent complex shear viscosity, $\eta(\nu)$, is approximated with the following Cole-Davidson function for quantitative analysis:

$$\eta(\upsilon) = \frac{\eta_P}{(1+2\pi i\tau\upsilon)^\beta}. \tag{1}$$

The plateau viscosity is described as η_P, τ is the parameter that gives the relaxation time, and β is associated with the distribution of the relaxation time. In this work, the value of β is fixed to be 0.5 for all the samples. The Cole-Davidson function is a representative model function to describe relaxations in viscous liquids, and we employed it in this work merely for the formal description. We tried the fitting with both $\beta = 0.5$ and 0.6, and the employed the results of the former because the fitting by the former was slightly better. We also confirmed that the discussion in this work is qualitatively the same using the fitting results of $\beta = 0.6$. The fitting curves of neat [bmim][TFSA] and PEG20k / [bmim][TFSA] solution are shown in Fig. 1, demonstrating that the Cole-Davidson function describes $\eta(\nu)$ except for the high-frequency edge of the

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polymer relaxation observed below 20 MHz in the polymer solution.

The shear relaxation spectra of other systems and their Cole-Davidson fittings are shown in Fig. S1 of Supporting Information, and the fitting parameters are summarized in Table S1 of Supporting Information. The fitting works well on all the ionic liquids and their polymer solutions. The AC conductivities of systems other than [bmim][TFSA] are also exhibited in Fig. S2 of Supporting Information.

The DC conductivity is calculated from the plateau of the real part of the AC conductivity in the MHz region, and converted into the molar DC conductivity, Λ_0, to extract the effects of polymer dissolution on ionic mobility. The molar concentration of ions is evaluated under the assumptions that the specific volume of PEG in ionic liquid is equal to that in water [21] and independent of the concentration of PEG.

The change in the physical properties on the dissolution of polymer is discussed based on the relative variation defined as

$$\Delta_{rel}(f) \equiv \frac{f_s - f_0}{f_0} \times 100, \tag{2}$$

where f_0 and f_s stand for the values of the property f in neat ionic liquids and the sample mixtures, respectively.
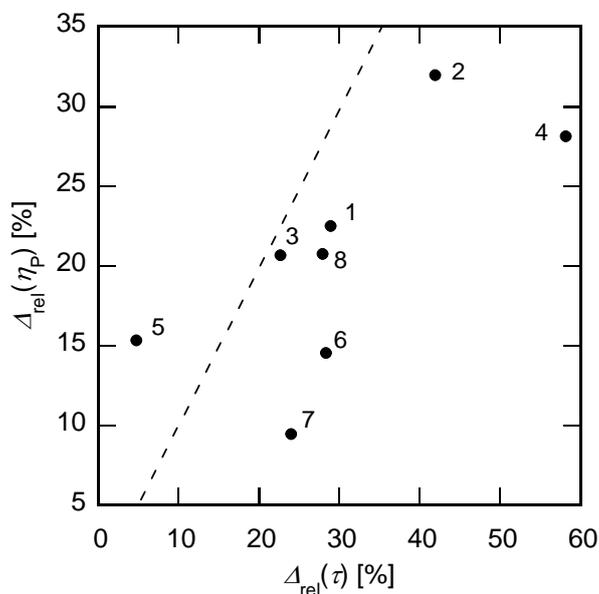

Figure 3.   The correlation between the relative variations of the relaxation time τ and the plateau viscosity, η_P.   The indexes indicate (1) [bmim][TFSA], (2) [bmim][PF$_6$], (3) [bmim][BF$_4$], (4) [emim][TFSA], (5) [omim][TFSA], (6) [bmmim][TFSA], (7) [bmpy][TFSA] and (8) [bpy][TFSA],

and the dashed line corresponds to $\Delta_{\text{rel}}(\tau) = \Delta_{\text{rel}}(\eta_P)$.

Figure 3 correlates the relative variations of the plateau viscosity and the relaxation time. Both quantities increase with the dissolution of PEG in all the ionic liquids used in this work. The relative increase in the plateau viscosity is qualitatively close to that in the relaxation time, and positive correlation between $\Delta_{\text{rel}}(\tau)$ and $\Delta_{\text{rel}}(\eta_P)$ exists. Provided that the shear viscosity is approximately proportional to the relaxation time of the shear stress, the positive correlation between $\Delta_{\text{rel}}(\tau)$ and $\Delta_{\text{rel}}(\eta_P)$ is quite natural, and the increase in the relaxation time can be regarded as a reason for that in the plateau viscosity. Quantitatively, the increase in the latter is smaller than that in the former except for [omim][TFSA], which suggests the decrease in the high-frequency shear modulus on polymer dissolution.
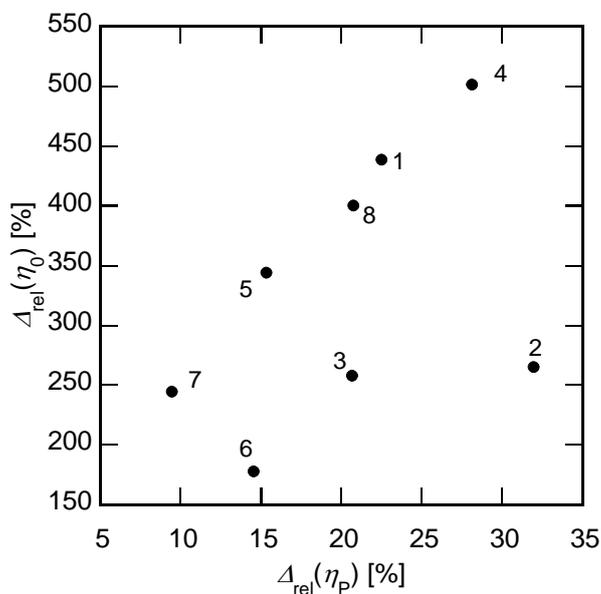

Figure 4. The correlation between the relative variations of the plateau viscosity, η_P, and the zero-frequency shear viscosity, η_0. The meanings of the indexes are the same as those in Fig. 3.

The correlation between the plateau and the zero-frequency viscosities, η_P and η_0, respectively, is exhibited in Fig. 4. We confirmed that the absolute values of η_P agree with those of η_0 in all the neat ionic liquids, indicating that no relaxation exists below 1 MHz in neat ionic liquids. On the other hand, η_P is far smaller than η_0 in all the polymer solutions as is demonstrated in Fig. 1 due to the contribution of slow polymer dynamics to the latter. As a result, the absolute values of $\Delta_{\text{rel}}(\eta_0)$ is much larger than those of $\Delta_{\text{rel}}(\eta_P)$ as is exhibited in Fig. 4.

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Liu and coworkers reported η_0 of the solutions of polyethylene oxide (PEO) in various ionic liquids including [bmim][PF$_6$] as the functions of the polymer concentration and the molecular weight [6]. According to the extrapolation of their experimental results, the transition between the linear and the square regime of the concentration dependence occurs around 3 g/ml at $M_w = 20000$. Kharel and Lodge estimated the overlap concentration of PEO in [bmim][BF$_4$] at 80 °C as 7.3 wt% and 4.3 wt% at the molecular weights of 10000 and 30000, respectively [9]. In the linear regime to the polymer concentration, shear viscosity of polymer solution is determined by the degree of the extension of a chain, which in turn reflects the strength of the attractive interaction between polymer and solvent. The more attractive between the polymer and the solvent, the more extended the polymer chain is, which leads to the larger value of shear viscosity. Since our experimental condition of 5 wt% is close to the overlap concentration, we consider that the zero-frequency viscosity is mainly determined by the extension of the single polymer chain.

In Fig. 4, we can find positive correlation between $\Delta_{\mathrm{rel}}(\eta_P)$ and $\Delta_{\mathrm{rel}}(\eta_0)$, although their absolute values are quite different from each other. The positive correlation can be naturally explained if we consider that both η_0 and η_P are controlled by the same kind of the attractive interaction between polymer and ions. The stronger interaction increases the former through the extension of the polymer chain, while it enhances the latter through the retardation of the structural relaxation.
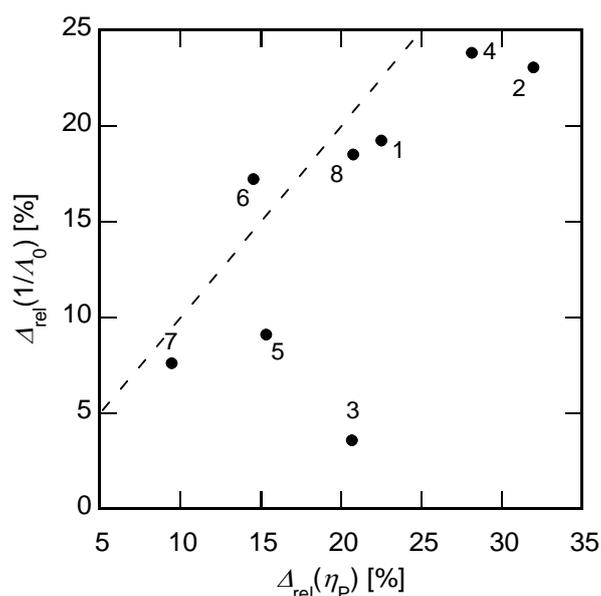

Figure 5. The correlation between the relative variations of the plateau viscosity, η_P, and the

inversed of the molar DC conductivity, $1/\Lambda_0$. The meanings of the indexes are the same as those in Fig. 3, and the dashed line corresponds to $\Delta_{rel}(1/\Lambda_0) = \Delta_{rel}(\eta_P)$.

The ionic mobility of ionic liquids is often treated in terms of the Walden rule, which is the reciprocal relation between the molar conductivity and the zero-frequency shear viscosity as [22,23,24]

$$\Lambda_0 \propto 1/\eta_0. \tag{3}$$

Figure 5 shows the correlation between the relative variations of η_P and $1/\Lambda_0$. The molar conductivity Λ_0 is inverted, considering its reciprocal proportionality to the shear viscosity predicted by eq. 3. The molecular mobility is retarded by the dissolution of PEG in all the ionic liquids as is demonstrated by the positive values of $\Delta_{rel}(1/\Lambda_0)$.

Comparing the absolute values of $\Delta_{rel}(1/\Lambda_0)$ in Fig. 5 with those of $\Delta_{rel}(\eta_0)$ in Fig. 4, however, the increase in the zero-frequency viscosity is much larger than the decrease in the molar conductivity, indicating the breakdown of the Walden rule. The failure of the Walden rule is easily understood in terms of the decoupling between the dynamic modes that governs these two quantities. The zero-frequency shear viscosity is dominated by the slow and large-scale motion of polymer chains, while ions migrate under the influence of microscopic ion-ion and ion-PEG interactions.

In Fig. 5, a positive correlation between $\Delta_{rel}(1/\Lambda_0)$ and $\Delta_{rel}(\eta_P)$ is clearly observed. In addition, their absolute values are also close to each other, although the latter is slightly larger than the former. It suggests that the Walden rule, eq. 3, holds also in the solutions of PEG in ionic liquids after the replacement of η_0 with η_P. In other words, the plateau viscosity can be regarded as the microscopic viscosity of ionic liquids around the polymer, and the ions in solution migrates under the influence of the microscopic viscosity.

The next question is how the plateau viscosity is related to the molecular structure and the microscopic interaction of the constituent ions. In this work, we focus on the hydrogen bonding between the cation and the ether oxygen atoms of PEG. It is well known that the C_2 proton of the imidazolium group behaves as a hydrogen-bond donor due to the large positive charge on the proton. Imidazolium-based ionic liquids was shown to be a good solvent of PEG, which was ascribed to the hydrogen bond between the cation and the oxygen of PEG [9]. The presence of the hydrogen bond was also demonstrated by a molecular

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dynamics (MD) simulation [25], X-ray diffraction [25] and nuclear magnetic resonance spectroscopy [26].

The Kamlet-Taft α is an empirical solvent parameter that describes the strength of the hydrogen-bond donating ability of solvents, which can be determined by the solvatochromism of two dye molecules, Betaine 30 and N-N-diethyl-4-nitroaniline [27]. The values of α of many ionic liquids have been reported in literatures so far [2,28,29], which will be used as a measure of the strength of the hydrogen bonding between PEG and ions.
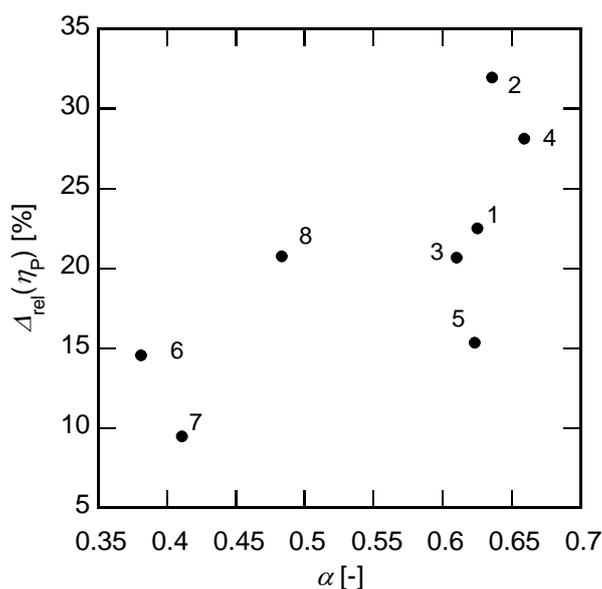

Figure 6.   The correlation between the Kamlet-Taft parameter α and the relative variation of the plateau viscosity, η_P.   The meanings of the indexes are the same as those in Fig. 3.

The correlation between α and $\Delta_{rel}(\eta_P)$ is shown in Fig. 6, where positive correlation between them is observed.   It suggests that the hydrogen-bonding interaction between PEG and ions plays a certain role in increasing the plateau viscosity.

In the series of anion variation, the change in α is small because the hydrogen-bond donating group is the same.   The order of α is (3) [bmim][BF$_4$] < (1) [bmim][TFSA] < (2) [bmim][PF$_6$], and $\Delta_{rel}(\eta_P)$ follows the same order.   Since the anions possess hydrogen-bond accepting ability, the hydrogen-bond interaction between the cation and the solute compete with that between the cation and the anion [28].   The weaker the hydrogen-bond accepting ability of the anion, the more favourable the formation of the hydrogen-bond between the cation and the polymer is, leading to the higher local viscosity of the ionic liquids.

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The increase in the alkyl chain length induces the decrease in α, although the variation of the latter is small. The longer alkyl group disfavours the hydrogen bond due to the steric hindrance and the decrease in the ionic concentration. In Fig. 6, the variation of $\Delta_{\mathrm{rel}}(\eta_{\mathrm{P}})$ in the series of (4) [emim][TFSA], (1) [bmim][TFSA] and (5) [omim][TFSA] seems larger than that expected from that of α, which we consider may be ascribed to the characteristic domain structure of ionic liquids. Ionic liquids with a long alkyl chain exhibit a mesoscale structure composed of polar and nonpolar domains, which has been demonstrated both by MD simulation [30] and diffraction experiment [31]. The hydrophobic ethylene group of PEG favours the nonpolar domain of ionic liquids, which may result in the large effect of the chain length on the plateau viscosity.

The substitution of the polar head group of the cation results in the large variation in α, because the head group is directly involved in the hydrogen bonding. The introduction of the methyl group into the C_2 position decreases α of (6) [bmmim][TFSA] compared with (1) [bmim][TFSA]. The reduction of the polymer-ion interaction on the methylation of the C_2 proton was also reported by Lee and coworkers [6], and our experimental results are consistent with theirs. The bulky aliphatic head group of (7) [bmpy][TFSA] also exhibits α as small as (6) [bmmim][TFSA]. The smaller number of nitrogen atoms of (8) [bpy][TFSA] reduces the hydrogen-bond donating ability of aromatic protons compared with (1) [bmim][TFSA].

However, the story may not be so simple because the strength of the correlation varies among the three series above. Both the variations of α and η_{P} are large in the last series. On the other hand, comparable variations of η_{P} are observed in the former two series with smaller changes in α. We thus consider that mechanisms other than the hydrogen-bond may also works in the former two series. The domain structure can be a possible candidate for the effects of the alkyl chain length as was already discussed above, and the direct interaction between PEG and anion may be present in the first series of the anion variation.

4.   Summary

The frequency-dependent complex shear viscosities of the solutions of PEG in various ionic liquids were determined experimentally, and the ionic conductivities of the same solutions were also investigated.　The effects of the PEG dissolution on various physicochemical quantities were analysed in terms of the relative variation between the neat liquid and the PEG solutions.

The plateau viscosity in the MHz region increased with the dissolution of PEG in all the ionic liquids investigated in this work, and it is ascribed at least partly to the retardation of the structural relaxation based on the correlation between the relative variations of the relaxation time and the plateau viscosity.　The increase in the plateau viscosity was also correlated with that in the zero-frequency viscosity, although the latter was much larger than the former.　The correlation between the viscosities at two different frequencies was explained as the effects of the same polymer-solvent attractive interaction.　The molar ionic conductivity decreased with the addition of PEG by the amount similar to the increase in the plateau viscosity, and these two values were also correlated with each other.　Therefore, the plateau viscosity of the solution of the polymer in ionic liquid can be regarded as the local viscosity effective to the ionic mobility.　The variation of the plateau viscosity correlated with the Kamlet-Taft α parameter particularly for the series of the variation of the head group of the cation, and the role of the polymer-cation hydrogen bond in increasing the local viscosity of ionic liquid was suggested.

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