# Quantitative Analysis of Conductivity and Viscosity of Ionic Liquids in Terms of Their Relaxation Times

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Ⓢ Supporting Information

ABSTRACT: The frequency-dependent viscosity and conductivity of various ionic liquids were measured experimentally, and their mean relaxation times were determined. The relaxation times of the viscosity and conductivity were approximately correlated with their respective zero-frequency limiting values. The Walden products, however, appeared to have no correlation with the ratio of the relaxation time of viscosity to that of conductivity in general. When the alkyl chain of the cation is as short as butyl, more viscous ionic liquids tend to show larger difference between two relaxation times and larger Walden products. Lengthening the alkyl chain of the cation decreases the Walden product while slightly increasing the relaxation time ratio, which was elucidated in terms of the decrease in the high-frequency shear modulus. In addition, the contribution of the mesoscopic structure to viscosity was suggested in the case of the ionic liquid with the longest alkyl chain studied in this work, 1-dodecyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide.
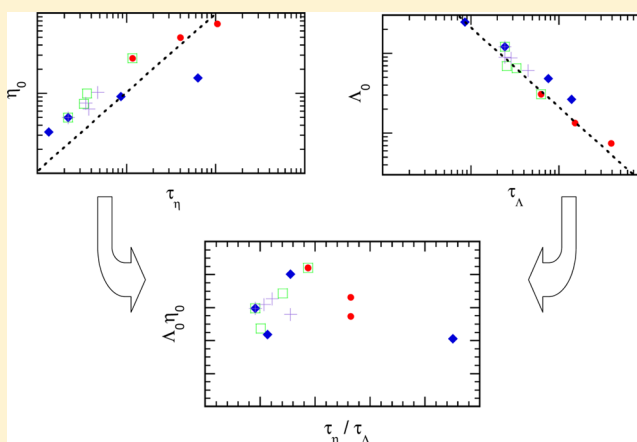
1. INTRODUCTION

The room-temperature ionic liquids, which are simply called "ionic liquids" nowadays, are studied intensively due to their potential use for electrochemical devices, reaction and separation media, and so on. The transport properties of ionic liquids such as ionic conductivity and shear viscosity are crucial properties for the practical uses, and these properties of various ionic liquids have thus been investigated extensively to date.[1−10]

The Walden law is an important relationship on ion-conducting fluids and states that the molar conductivity of ions is inversely proportional to the shear viscosity.[11,12] The Walden product is defined as the product of shear viscosity and molar conductivity, and the Walden law can be described in other words that the Walden product is constant. In the case of ionic liquids, the "Walden plot" is often used in the analysis of ionic conductivity.[13−15] The Walden plot is the log−log plot between the molar conductivity and reciprocal shear viscosity (fluidity). The correlation between the molar conductivity and the reciprocal shear viscosity should lie on the line with a slope of unity when the Walden law holds.

Transport properties of liquids are determined by the dynamics of liquids.[16] The steady-state shear viscosity, η_0, for instance, is approximately described as the product of the shear relaxation time, τ_η, and the high-frequency limiting shear modulus, G_∞.[12,17] Given that the variation of G_∞ is usually much smaller than that of τ_η, the steady-state shear viscosity is

approximately proportional to the relaxation time, τ_η. Similarly, the direct current (DC) molar conductivity, Λ_0, is approximately proportional to the reciprocal value of the relaxation time, τ_Λ, which is usually interpreted as the hopping time or the relaxation time of the structure coupled with the translational motion of ions.

The Walden law can be regarded as the relationship between the relaxation times of the shear viscosity and molar conductivity. When the translational ionic motion and the shear flow of the bulk liquid are coupled with the same kind of liquid structure, the relaxation times are equal, $\tau_\eta = \tau_\Lambda$, reflecting the relaxation time of the liquid structure. Provided that the relaxation times are proportional to both η_0 and $1/\Lambda_0$, $\tau_\eta = \tau_\Lambda$ can be a reason for the reciprocal proportionality between η_0 and Λ_0. Therefore, the Walden product has been regarded as a measure of the coupling between the mechanisms that determine η_0 and Λ_0, respectively.

The view of the Walden law as the relationship between relaxation times originates in the study on the slow dynamics of supercooled liquids. Approaching the glass transition temperature with cooling, supercooled liquids experience a rapid increase in the relaxation times, thereby increasing their shear viscosity and decreasing their self-diffusion coefficients

accordingly. One important issue is the relationship between the shear viscosity and the self-diffusion coefficient.[18] In liquids at temperatures much higher than the glass transition temperature, the Stokes−Einstein relationship, which states that the self-diffusion coefficient is reciprocally proportional to the shear viscosity, is considered to hold approximately. On the other hand, the decrease in the self-diffusivity upon cooling is much smaller than that expected from the Stokes−Einstein relationship in supercooled liquids near the glass transition temperature. The shear viscosity is proportional to the relaxation time as was described above. The self-diffusion coefficient is reciprocally proportional to the associated relaxation time, as is the case of the molar conductivity. Therefore, the violation of the Stokes−Einstein relationship can be regarded as the difference between these two relaxation times. Recent computer simulations show that such a difference between the relaxation times actually occurs in models of supercooled liquid.[19,20]

The relationship between the Walden law and the two relaxation times holds when the variation of the proportionality coefficient between the transport coefficient and the relaxation time, G_∞, for instance, is much smaller than that of the Walden product. Such a condition is actually satisfied in the case of supercooled liquids, where the variation of the shear viscosity spans more than 10 decades near the glass transition temperature. However, the changes in the quantities of ionic liquids in which many chemists are interested are usually much smaller. For example, the absolute values of η_0 usually lie between 0.01 and 10 Pa·s, and the variation of the Walden product is typically within a factor of 2, which is comparable to the variation of G_∞ of nonionic liquids.[17] We should thus be careful before applying the discussion on supercooled liquids to ionic liquids in a naive way.

The relaxation time associated with a transport property can be determined experimentally with the measurement of the frequency-dependence of the transport coefficient. The frequency-dependent electric conductivities of various ionic liquids have been determined using dielectric spectroscopy to clarify the ionic conduction mechanism.[21−24] Although the number of studies on the viscoelastic relaxation of ionic liquids is relatively small,[25−30] the viscoelastic spectra of some ionic liquids have been compared with the conductivity spectra to examine the relationship between η_0 and Λ_0.[31−33] In particular, we have investigated in our previous work the frequency-dependent viscosity and conductivity of a series of 1-alkyl-3-methylimidazolium hexafluorophosphate with varying lengths of the alkyl chain, and we demonstrated that the decrease in the Walden product with an increase in the chain length is ascribed to the decrease in G_∞.[32] In this work, we shall extend our previous work to various kinds of ionic liquids to understand the relationship between the shear viscosity, molar conductivity, and the relaxation times associated with them.

There have been many theoretical and computer simulation studies on the transport properties of ionic liquids. In most of these studies, the time correlation functions associated with the transport properties were calculated first, and then the transport coefficients were evaluated from the time correlation function. The comparison with experiments, however, was performed merely on the zero-frequency values of the transport coefficients in most cases. Because the relaxation spectra determined in this work are essentially equivalent to the time correlation functions, as will be described in the next section, the experimental spectra in this work shall provide more severe examination of theoretical and computational works.

2. THEORETICAL BACKGROUND

According to the Kubo−Green formula, the frequency-dependent complex shear viscosity, $\eta(\nu)$, is related to the time-correlation function of the shear stress tensor, $C_\eta(t)$, as

$$\eta(\nu) \equiv \frac{V}{k_B T} \int_0^\infty d\tau\, e^{-2\pi i \nu \tau} C_\eta(\tau) \tag{1}$$

where V, T, and k_B are the volume of the system, the absolute temperature, and the Boltzmann constant, respectively. In particular, the steady-state shear viscosity, η_0, is described as the time integral of the correlation function as

$$\eta_0 \equiv \eta(0) = \frac{V}{k_B T} \int_0^\infty d\tau C_\eta(\tau) \tag{2}$$

Equation 1 indicates that $\eta(\nu)$ is frequency-dependent in the frequency region corresponding to the reciprocal relaxation time of $C_\eta(t)$, denoted as τ_η, and eq 2 indicates that η_0 is proportional to τ_η.

The alternating-current (AC) electric conductivity, $\sigma(\nu)$, is described in terms of the time-correlation function of the electric current, $C_J(t)$, as

$$\sigma(\nu) \equiv \frac{V}{k_B T} \int_0^\infty d\tau\, e^{-2\pi i \nu \tau} C_J(\tau) + 2\pi i \varepsilon_0 \nu \tag{3}$$

$$C_J(t) \equiv \frac{1}{3} \langle j_e(0) \cdot j_e(t) \rangle \tag{4}$$

where ε_0 and $j_e(t)$ are the dielectric constant of vacuum and the electric current density, respectively.

Although the DC electric conductivity, $\sigma_0 \equiv \sigma(0)$, is determined exclusively by the translational motion of ions, there are at least two other sources of the electric current density that may contribute to the AC conductivity. The first one is the electronic polarization of ions. Provided that the frequency range studied in this work is far lower than that of the electronic transition, the contribution of the electronic polarization to the AC conductivity is approximated in this work as

$$\sigma_{el}(\nu) \cong 2\pi i (n^2 - 1) \varepsilon_0 \nu \tag{5}$$

where n denotes the refractivity index measured with visible light.

The second additional source of the electric current density is the reorientational motion of ions. Because most ionic liquids contain asymmetric ions to lower melting temperature, the rotation of the asymmetric ions around the center-of-mass causes a transient electric current. There have been three ways so far to analyze the frequency-dependent conductivity of ionic liquids. The first one is to assume that the contribution of the translational mode is independent of frequency, assigning the whole frequency-dependent part to the reorientational relaxation.[34−40] However, computer simulation studies and theoretical consideration have demonstrated that the translational mobility must depend on frequency in the frequency region where the slowest relaxation of $\sigma(\nu)$ is observed.[41−44] The second one is to divide various contributions by a curve fitting procedure.[21] Though this kind of analysis is more appropriate than the other two methods in that both translational and reorientational modes are taken into account,

the resultant division may depend crucially on the choice of the model functions. The third way is to neglect the contribution of the reorientational relaxation,[31,32] which is the method we employ in this work. The dipole moment of a charged molecule (molecular ion) is dependent on the choice of the center, and we can choose the molecular center around which its dipole moment vanishes. The "translational" motion of ions we discuss in this work refers to the motion of such molecular centers because the reorientational motion around them cannot be a source of the transient electric current.

Under the assumption that the AC conductivity is given by the sum of the contributions of the electronic polarization and the translational motion of ions, the latter, denoted as $\sigma_I(\nu)$, is evaluated by the equation as follows:

$$\sigma_I(\nu) = \sigma(\nu) - 2\pi i n^2 \varepsilon_0 \nu \qquad (6)$$

In the diffusive limit where the inertia of ions is neglected, the frequency-dependent ionic conductivity, $\sigma_I(\nu)$, is reciprocally proportional to the generalized friction coefficient, $\zeta(\nu)$, as

$$\sigma_I(\nu) \propto \frac{1}{\zeta(\nu)} \qquad (7)$$

and $\zeta(\nu)$ is described in terms of the time-correlation function of the random force, $C_R(t)$, as

$$\zeta(\nu) \propto \int_0^\infty d\tau \, e^{-2\pi i \nu \tau} C_R(\tau) \qquad (8)$$

In particular, the DC molar conductivity, $\Lambda_0 \equiv \sigma_I(0)/c$ (c stands for the molar concentration of ions), is reciprocally proportional to the relaxation time of $C_R(t)$, denoted as τ_Λ, as

$$\Lambda_0 = \frac{1}{Z_\Lambda \tau_\Lambda} \qquad (9)$$

where Z_Λ indicates the proportionality coefficient.

It is to be noted here that the random force, R, associated with $\zeta(\nu)$ in eq 8, is on the collective electric current rather than on individual ions. The self-part of the correlation function of the random force is related to the friction on the translational motion of an ion, which determines the frequency-dependent self-diffusion coefficient of the ion, $D(\nu)$. The presence of the cross correlation between random forces on different ions is easily observed as the breakdown of the Nernst−Einstein relationship between the DC conductivity and the self-diffusion coefficients of ions, and the meaning of the cross correlation has been intensively discussed.[13,45] We have also calculated both $\sigma_I(\nu)$ and $D(\nu)$ of a model ionic liquid by using mode-coupling theory (MCT) and molecular dynamics (MD) simulation, and demonstrated that the relaxation of the former is faster than that of the latter.[41,42] However, we shall not pursue the issue of the cross correlation in this work because experimental determination of $D(\nu)$ is not performed.

The two time correlation functions described above, $C_\eta(t)$ and $C_R(t)$, are proportional to each other when the liquid dynamics that determine the shear viscosity and the ionic conductivity are the same. In such a case, the two relaxation times, τ_η and τ_Λ, are equal to each other, and Λ_0 is reciprocally proportional to η. The Walden product is therefore used as the coupling between the shear viscosity and the ionic conductivity under the assumption that the variation of the two proportionality coefficients, G_∞ and Z_Λ, is small. However, because the relaxation time directly reflects the transport

mechanisms, the discussion on the coupling between shear viscosity and ionic conductivity is better performed on the basis of the relaxation measurements.

Provided that the shear stress and the random force on the collective electric current are different physical quantities, their time correlation functions, $C_\eta(t)$ and $C_R(t)$, can in principle possess different relaxation times. The simplest view that τ_η and τ_Λ are equal to each other is suggested by MCT, where $C_\eta(t)$ and $C_R(t)$ are described by the linear combination of the bilinear product of the intermediate scattering function.[41,46] Because the time dependence of these correlation functions are governed in cases of dense liquids by the dynamics at the wavenumber where the principal peak of the structure factor exists,[46] MCT predicts similar values for the two relaxation times. We also confirmed that τ_η and τ_Λ have similar values within the MCT approximation, though the numerical results were not shown in ref 41. The difference between these two relaxation times thus suggests the breakdown of the simplest MCT view in a sense.

In the numerical analysis of this work, we approximate the spectra, $\eta(\nu)$ or $1/\sigma_I(\nu)$, as the summation of a Cole−Davidson function and a Debye function as

$$\eta(\nu), \frac{1}{\sigma_I(\nu)} \cong \frac{A_1}{(1 + 2\pi i \nu \tau_1)^\beta} + \frac{A_2}{1 + 2\pi i \nu \tau_2} \qquad (10)$$

where τ_2 is smaller than τ_1. The Debye function is introduced only when a Cole−Davidson function alone cannot reproduce the spectrum. The mean relaxation time, denoted as $\langle \tau \rangle$, of the time correlation function $C(t)$ is defined as

$$\langle \tau \rangle \equiv \int_0^\infty \tau C(\tau) \, d\tau \Big/ \int_0^\infty C(\tau) \, d\tau \qquad (11)$$

which is related to the parameters in eq 10 as

$$\langle \tau \rangle = \frac{A_1 \beta \tau_1 + A_2 \tau_2}{A_1 + A_2} \qquad (12)$$

Hereafter, we shall denote $\langle \tau \rangle$ associated with $C_\eta(t)$ and $C_R(t)$ as τ_η and τ_Λ, respectively.

2. EXPERIMENTAL SECTION

2.1. Samples. We studied four series of ionic liquids in this work. In the first one, the cation was kept as 1-butyl-3-methylimidazolium (bmim$^+$), and the anion was varied as hexafluorophosphate (PF_6^-), bis(trifluoromethanesulfonyl)-amide (TFSA$^-$), tetrafluoroborate (BF_4^-), and trifluoroacetate (TFA$^-$). In the second series, the anion was TFSA$^-$, while the cations were bmim$^+$, 1-butyl-3-methylpyridinium (bmpyr$^+$), N-butyl-N-methylpyrrolidinium (bmpro$^+$), and butyltrimethylammonium (btma$^+$). The cations were chosen so that the lengths of the alkyl chains were the same. In the remaining two series, the anions were kept as PF_6^- or TFSA$^-$, respectively, and the cation was 1-alkyl-3-methylimidazolium (C$_n$mim$^+$), where n is the number of the carbon atoms of the longest alkyl chain. The values of n employed were 4, 6 (hmim$^+$), and 8 (omim$^+$) for the PF_6^- series, and 2 (emim$^+$), 4, 8, and 12 (domim$^+$) for the TFSA$^-$ series. The suppliers of the samples are given in Table S1 (Supporting Information). All the samples were dried at 60 °C under vacuum prior to use, and the values of water content, determined with a Kirl−Fisher Coulometer (Metrohm, 831 KF), were below 300 ppm, except for that of [bmim][TFA] (900 ppm). The presence of 1000 ppm water may result in the increase of conductivity by 3−5%,[47] which is sufficiently small

compared with the variations of quantities discussed in this work. The densities of the samples used for analysis were taken from literatures and summarized in Table S1 (Supporting Information).

2.2. Viscometry. The frequency-dependent shear viscosity was measured with a homemade shear impedance spectrometer,[48] which was described in detail elsewhere.[49−51] Briefly, the electric responses of an AT-cut quartz crystal before and after the contact with sample liquids are measured using a vector network analyzer (VNA; Rhode-Schwarz, ZVL3/03), and the viscous friction onto the crystal was determined. The frequency range of the measurement was 5−205 MHz with intervals of 5 MHz. The temperature was controlled at 25.0 ± 0.1 °C by flowing thermostated water through the sample cell. The measurements were performed twice for each sample liquid. The two spectra were averaged after confirming the reproducibility within the experimental error.

The values of η_0 are summarized in Table S2 (Supporting Information). Some of them were taken from literatures, while others were determined with a cone−plate viscometer (RVDV-IPCP, Brookfield) equipped with a spindle CPE-40.

2.3. Conductometry. The frequency-dependent conductivity was measured with the dielectric spectroscopy using a VNA (Rhode−Schwarz, ZVL3/03), a detailed explanation for which is given in a literature.[32] The sample liquids were held in a coaxial cell made of an aluminum body and an SMA panel receptacle, and the electric impedance between the signal pin of the panel receptacle and the aluminum body was determined. The electric impedances of the connectors were approximated as the equivalent circuit shown in a literature,[50] and the parameters of the circuits were determined by measuring the electric impedance spectra with air, water, and aqueous solutions of sodium chloride.[52] The spectral range of the measurement was 300 kHz−700 MHz. All the measurements were performed at 25.0 ± 0.1 °C. The measurements were performed twice, and the averaged spectra were used for analysis. The values of σ_0 were determined from the plateau values of the real part of $\sigma(\nu)$ around 1 MHz and tabulated in Table S2 (Supporting Information).

The refractive indices required in the analysis of $\sigma(\nu)$ were measured with an Abbe refractometer (Erma, 17151). These values are also tabulated in Table S1 (Supporting Information).

3. RESULTS AND DISCUSSION

The relaxation functions $\eta(\nu)$ and $1/\sigma_I(\nu)$ are exhibited in Figures S1−S12 (Supporting Information). Some of these spectra are not new but are taken from our previous works as described in the captions of these figures. The model functions (eq 10) with the optimized parameters are plotted together there for comparison. The model functions reproduce the experimental spectra well. The mean relaxation times evaluated with these parameters are tabulated in Table S2 (Supporting Information). The values of DC conductivity, σ_0, determined from the conductivity spectra are compared with those in literatures in Table S2 (Supporting Information). The difference between the values in this work and in literatures is comparable to the variation among values in literatures.

Figure 1 exhibits the correlation between η_0 and τ_η for all the samples studied in this work. These two values are proportional to each other when the length of the alkyl chain of cations is not larger than butyl, as is expected when the high-frequency shear modulus, G_∞, does not depend on ionic species.
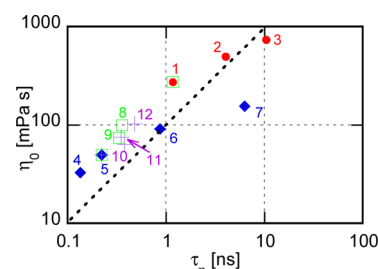

Figure 1. Correlation between the shear relaxation time, τ_η, and the steady-state shear viscosity, η_0. The values of the series of 1-alkyl-3-methylimidazolium cations with PF_6^- and $TFSA^-$ anions are shown with red circles and blue diamonds, respectively, and those of the series of bmim$^+$ and TFSA$^-$ salts are with green squares and purple crosses, respectively. The samples are 1, [bmim][PF_6]; 2, [hmim]-[PF_6]; 3, [omim][PF_6]; 4, [emim][TFSA]; 5, [bmim][TFSA]; 6, [omim][TFSA]; 7, [domim][TFSA]; 8, [bmim][BF_4]; 9, [bmim]-[TFA]; 10, [bmpyr][TFSA]; 11, [bmpro][TFSA]; and 12, [btma]-[TFSA]. The black dotted line, the slope of which is unity, is drawn as a guide.

In our recent study on the shear relaxation of lubrication oils, we showed that the presence of ring groups, either phenyl or cyclohexyl ones, increases G_∞.[53] However, comparing the TFSA$^-$ salts with cyclic cations ([bmim][TFSA], [bmpyr]-[TFSA], and [bmpro][TFSA]) to the salt without a cyclic cation ([btma][TFSA]), no meaningful difference is found in their ratios of η_0 to τ_η. It can be ascribed to the difference in the intermolecular interactions that determine the shear viscosity of lubrication oils and ionic liquids because strong Coulombic interaction exists in the latter.

The correlation between Λ_0 and τ_Λ is demonstrated in Figure 2. The reciprocal proportionality predicted by eq 9 holds
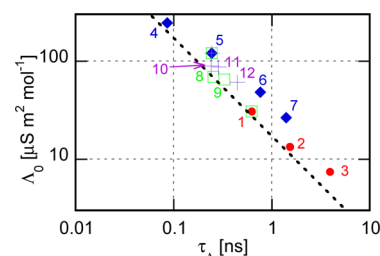

Figure 2. Correlation between the conductivity relaxation time, τ_Λ, and the DC molar conductivity, Λ_0. The values of the series of 1-alkyl-3-methylimidazolium cations with PF_6^- and TFSA$^-$ anions are shown with red circles and blue diamonds, respectively, and those of the series of bmim$^+$ and TFSA$^-$ salts are with green squares and purple crosses, respectively. The samples are 1, [bmim][PF_6]; 2, [hmim]-[PF_6]; 3, [omim][PF_6]; 4, [emim][TFSA]; 5, [bmim][TFSA]; 6, [omim][TFSA]; 7, [domim][TFSA]; 8, [bmim][BF_4]; 9, [bmim]-[TFA]; 10, [bmpyr][TFSA]; 11, [bmpro][TFSA]; and 12, [btma]-[TFSA]. The slope of the black dotted line is −1.

approximately, as is the case of viscosity demonstrated in Figure 1. It can thus be said safely that the relaxation time, τ_Λ, is the principal factor that governs Λ_0. The reciprocal proportionality between Λ_0 and τ_Λ was already demonstrated by Sangoro and Kremer for wide temperature range.[32] We compared the conductivity and viscosity, and the correlation is better for the former than for the latter.

The increase in η_0 with lengthening the alkyl chain is larger than that of τ_η, which means that G_∞ is the decreasing function

of the chain length. We have demonstrated the deviation from the proportionality qualitatively in our previous work on PF_6^- salts,[32] and the deviation is demonstrated quantitatively and on $TFSA^-$ salts in this work.

The reciprocal proportionality between Λ_0 and τ_Λ is also violated by increasing the alkyl chain length, namely, the decrease in Λ_0 with an increase the chain length is smaller than that expected from the increase in τ_Λ, though the degree of the violation is smaller than that between η_0 and τ_η. The qualitative analysis in our previous work showed that Λ_0 was approximately proportional to $1/\tau_\Lambda$ because the deviation from the proportionality is not large enough to be detected by the qualitative analysis.

Figure 3 exhibits the relationship between the two relaxation times, τ_Λ and τ_η. They are expected to agree with each other, as
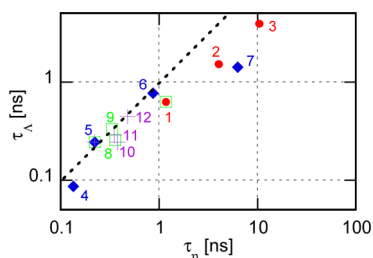
Figure 3. Correlation between the relaxation times of conductivity and viscosity, τ_Λ and τ_η, respectively. The values of the series of 1-alkyl-3-methylimidazolium cations with PF_6^- and $TFSA^-$ anions are shown with red circles and blue diamonds, respectively, and those of the series of bmim$^+$ and $TFSA^-$ salts are with green squares and purple crosses, respectively. The samples are 1, [bmim][PF_6]; 2, [hmim]-[PF_6]; 3, [omim][PF_6]; 4, [emim][TFSA]; 5, [bmim][TFSA]; 6, [omim][TFSA]; 7, [domim][TFSA]; 8, [bmim][BF_4]; 9, [bmim]-[TFA]; 10, [bmpyr][TFSA]; 11, [bmpro][TFSA]; and 12, [btma]-[TFSA]. The black dotted line is the line on which these two relaxation times are equal to each other.

is shown with the black dotted line, when the shear viscosity and ionic conductivity are determined by the same liquid dynamics. Although these two relaxation times vary in the same direction with changing the ionic species, their absolute values are not equal in general. The values of τ_Λ are not larger than those of τ_η within the experimental errors, and their deviation is likely to grow with increasing these relaxation times except for [emim][TFSA].

Figure 3 is equivalent to the Walden plot if the values of G_∞ and Z_Λ are independent of ionic species, and the dotted line should correspond to the so-called "ideal line" in principle. The τ_Λ value smaller than that of τ_η means the ionic conduction time is faster than the ideal conduction time. In the commonly used Walden plot, however, the values of Λ_0 of most ionic liquids are smaller than those predicted by the so-called "ideal line" determined with the aqueous solution of KCl, which we consider is because the ionic conduction of KCl in water cannot be used as the ideal behavior of ionic liquids, as was discussed in some literatures.[54,55]

Computer simulation studies on model supercooled liquids have demonstrated that the increase in τ_η upon cooling is stronger than that in the relaxation time associated with self-diffusion, which is the reason for the breakdown of the Stokes–Einstein relationship.[19,20] Supposing that the relaxation time for the self-diffusion is equivalent to that for the ionic conduction, the tendency of the larger difference between τ_Λ and τ_η of ionic

liquids with longer relaxation times is similar to that revealed computationally on supercooled liquids.

The slower relaxation time of viscosity than that of conductivity has already been reported by Šantić and co-workers on supercooled ionic liquids,[31] and we have also reported on [bmim][PF_6] at room temperature.[25] Figure 3 demonstrates that the decoupling between the relaxations of viscosity and ionic mobility is rather general behavior of ionic liquids above melting temperature.

One may consider that, because the decoupling between the shear viscosity and the translational diffusion is characteristic to supercooled liquids, it is not expected to occur in ionic liquids with temperatures higher than their melting points. However, there have been some studies that demonstrate that the dynamics of ionic liquids above the melting temperature show slow dynamics common to supercooled liquids. For example, computer simulation studies showed the dynamic heterogeneiry and the subdiffusive behavior of the mean-square displacement of ions.[56−60]

Considering that the decoupling between the shear viscosity and the translational mobility is one of the characteristics of supercooled liquids, temperature can be an important parameter to understand the decoupling observed in our experiment. The fractional dependence of the molar conductivity, which is common to supercooled liquids, was already reported by Harris and co-workers,[61] which suggests that the decoupling becomes stronger upon cooling. Although our experiments were performed at a fixed temperature due to the limitation of our experimental facilities, it would be more desirable to perform comparison using some kinds of reduced temperature such as T/T_g, where T_g stands for the glass transition temperature. In Figure 3, the decoupling tends to become larger for ionic liquids with longer relaxation times. Because ionic liquids with longer relaxation times are likely to possess higher T_g, the values of the reduced temperature, T/T_g, become lower, which can be a reason for the larger decoupling between τ_Λ and τ_η.

The relationship between the Walden product and the relaxation time ratio is demonstrated in Figure 4. There seems
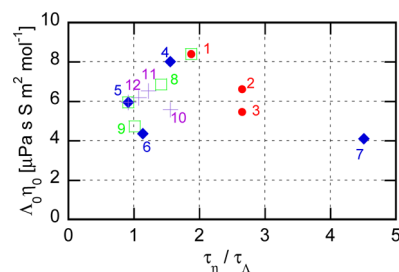

Figure 4. Correlation between the Walden product, $\Lambda_0\eta_0$, and the ratio of the relaxation time of shear viscosity to that of molar conductivity, τ_η/τ_Λ. The values of the series of 1-alkyl-3-methyl-imidazolium cations with PF_6^- and $TFSA^-$ anions are shown with red circles and blue diamonds, respectively, and those of the series of bmim$^+$ and $TFSA^-$ salts are with green squares and purple crosses, respectively. The samples are 1, [bmim][PF_6]; 2, [hmim][PF_6]; 3, [omim][PF_6]; 4, [emim][TFSA]; 5, [bmim][TFSA]; 6, [omim]-[TFSA]; 7, [domim][TFSA]; 8, [bmim][BF_4]; 9, [bmim][TFA]; 10, [bmpyr][TFSA]; 11, [bmpro][TFSA]; and 12, [btma][TFSA]. The so-called "ideal line" determined with the aqueous solution of KCl corresponds to the horizontal line at the top of the plot, $\Lambda_0\eta_0 = 10$ $\mu Pa\cdot s\ S\cdot m^2\cdot mol^{-1}$.

to be no correlation between them at a glance. Therefore, the Walden product cannot be a measure of the coupling between the dynamics that determine the shear viscosity and the ionic mobility. When we look closely, the expected proportionality may be observed approximately for ionic liquids with butyl groups (green squares and purple crosses). However, the deviation from the proportionality is considerably large, indicating that there are many other factors that are reflected in the Walden product.

When the alkyl chains of the PF_6^- and $TFSA^-$ salts are lengthened from butyl ($n = 4$) to octyl ($n = 8$), the Walden product decreases, while the ratio of the relaxation times increases slightly, which indicates that the decrease in G_∞ is the principal reason for that in the Walden product as we proposed in our previous work. Computer simulation and diffraction studies demonstrated that ionic liquids with long alkyl chain show a mesoscopic structure in which ionic and nonpolar domains are separated microscopically.[62-66] The lengthening of the alkyl chain increases the volume of the nonpolar domain, which weakens the interionic interaction on average, to which the decrease in G_∞ was ascribed. The effects of the nonpolar domain on Z_Λ would be smaller if the translational motion of ions were affected by the interionic interaction and the liquid dynamics within the ionic domain. We consider that the different roles of the mesoscopic structure on G_∞ and Z_Λ are the reason for the decrease in the Walden product with lengthening the alkyl chain.

The ionic liquid with the longest alkyl chain in this work, [domim][TFSA], shows a great difference between τ_Λ and τ_η, which suggests the different mechanisms for the shear viscosity and the ionic mobility. The deviation from the proportionality between η_0 and τ_η is large for [domim][TFSA], while that between Λ_0 and τ_Λ is small, suggesting that the mechanism for the shear viscosity is responsible for the greater difference between τ_Λ and τ_η. Rocha and co-workers recently measured the viscosity of 1,3-dialkylimidazolium TFSA when varying the lengths of the alkyl chains separately.[66] When the total lengths of the two chains is smaller than 12, the viscosity grows with increasing the total chain lengths similarly irrespective of the asymmetry of the lengths of the two chains. On the other hand, the increase in η_0 of [$C_n$mim][TFSA] as the function of n becomes rapid at $n \geq 12$ compared with that of the ionic liquids which have two alkyl chains of the length of $n/2$. Their experimental results thus suggest the presence of an additional mechanism that increases η_0 of [$C_n$mim][TFSA] of $n \geq 12$. At the same time, they demonstrated that [$C_n$mim][TFSA]s of $n \geq 12$ possess pronounced mesoscopic structure, which is scarcely observed for the ionic liquids of symmetric chain lengths. Therefore, the coupling between the shear flow and the mesoscopic structure can be a candidate that elucidates the large difference between τ_Λ and τ_η.

Yamamuro and co-workers determined the structural relaxation times associated with the mesoscopic structure and the microscopic one within the ionic domain using neutron spin echo spectroscopy.[67,68] They demonstrated that the relaxation time of the former is about one order of magnitude longer than that of the latter. In our previous work, we compared our shear relaxation spectra with these structural relaxations and found that the shear relaxation time is between these two relaxation times.[69] We thus concluded that the shear viscosity of these ionic liquids is not ascribed to the dynamics of the mesoscopic structure alone. In addition, we proposed two possible explanations for the slower shear relaxation than the

microscopic structural relaxation. The first one is the mechanism common to supercooled liquids in general, which was already described in the discussion on Figure 3. The second one is that the contribution of the mesoscopic relaxation is superposed on the shear relaxation. We consider that the second mechanism is a reason for τ_η being larger than τ_Λ in the case of [domim][TFSA], that is, the dynamics of the mesoscopic structure is coupled with the shear stress to retard the mean shear relaxation time but has little impact on the ionic conduction.

4. SUMMARY

The frequency-dependent shear viscosity and ionic conductivity of various ionic liquids were measured experimentally, and their mean relaxation times were determined. The relaxation times, τ_Λ and τ_η, are approximately correlated with the corresponding zero-frequency values of the transport coefficients, Λ_0 and η_0, respectively. The correlation is better for conductivity than for viscosity and worse for liquids with longer alkyl chains.

When the alkyl chains of the cations are as short as butyl, the two relaxation times of less viscous ionic liquids are comparable to each other. The ratio of τ_η to τ_Λ tends to increase with an increase in the viscosity of the liquids, and the Walden product also increases with viscosity. The mechanism of the deviation is thus considered to be common to that of supercooled liquids in general, which has been originally introduced to elucidate the breakdown of the Stokes−Einstein relationship. However, the correlation between the relaxation time ratio and the Walden product is not so good, indicating that the latter is not determined solely by the former.

The increase in viscosity with increasing the chain length from butyl to octyl is larger than the shear relaxation time, which means that the high-frequency shear modulus, G_∞, is a decreasing function of the chain length. The decrease in G_∞ is also responsible to the decrease in the Walden product with slight increase in the relaxation time ratio.

The ionic liquid with the longest alkyl chain in this work, [domim][TFSA], shows the relaxation time of viscosity far larger than that of conductivity, which is ascribed to the coupling between the shear stress and the dynamics of mesoscopic structure characteristic to ionic liquids with long alkyl chains.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

Physicochemical properties, relaxation parameters, and the relaxation spectra of ionic liquids. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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■ REFERENCES

(1) Weingärtner, H. Understanding Ionic Liquids at the Molecular Level: Facts, Problems, and Controversies. *Angew. Chem., Int. Ed.* **2008**, *47*, 654−670.

(2) Tokuda, H.; Tsuzuki, S.; Susan, M. A. B. H.; Hayamizu, K.; Watanabe, M. How Ionic Are Room-Temperature Ionic Liquids? An Indicator of the Physicochemical Properties. *J. Phys. Chem. B* **2006**, *110*, 19593−19600.

(3) Ueno, K.; Tokuda, H.; Watanabe, M. Ionicity in Ionic Liquids: Correlation with Ionic Structure and Physicochemical Properties. *Phys. Chem. Chem. Phys.* **2010**, *12*, 1649−1658.

(4) Harris, K. R.; Woolf, L. A.; Kanakubo, M. Temperature and Pressure Dependence of the Viscosity of the Ionic Liquid 1-Butyl-3-methylimidazolium Hexafluorophosphate. *J. Chem. Eng. Data* **2005**, *50*, 1777−1782.

(5) Harris, K. R.; Kanakubo, M.; Woolf, L. A. Temperature and Pressure Dependence of the Viscosity of the Ionic Liquids 1-Methyl-3-octylimidazolium Hexafluorophosphate and 1-Methyl-3-octylimidazolium Tetrafluoroborate. *J. Chem. Eng. Data* **2006**, *51*, 1161−1167.

(6) Harris, K. R.; Kanakubo, M.; Woolf, L. A. Temperature and Pressure Dependence of the Viscosity of the Ionic Liquids 1-Hexyl-3-methylimidazolium Hexafluorophosphate and 1-Butyl-3-methylimidazolium Bis(trifluoromethylsulfonyl)imide. *J. Chem. Eng. Data* **2007**, *52*, 1080−1085.

(7) Harris, K. R.; Kanakubo, M. High Pressure Studies of the Transport Properties of Ionic Liquids. *Faraday Discuss.* **2012**, *154*, 425−438.

(8) Stoppa, A.; Zech, O.; Kunz, W.; Buchner, R. The Conductivity of Imidazolium-Based Ionic Liquids from (−35 to 195) °C. A. Variation of Cation's Alkyl Chain. *J. Chem. Eng. Data* **2010**, *55*, 1768−1773.

(9) Zech, O.; Stoppa, A.; Buchner, R.; Kunz, W. The Conductivity of Imidazolium-Based Ionic Liquids from (248 to 468) K. B. Variation of the Anion. *J. Chem. Eng. Data* **2010**, *55*, 1774−1778.

(10) Seki, S.; Kobayashi, T.; Kobayashi, Y.; Takei, K.; Miyashiro, H.; Hayamizu, K.; Tsuzuki, S.; Mitsugi, T.; Umebayashi, Y. Effects of Cation and Anion on Physical Properties of Room-Temperature Ionic Liquids. *J. Mol. Liq.* **2010**, *152*, 9−13.

(11) Bockris, J. O'M.; Reddy, A. K. N. *Modern Electrochemistry 1: Ionics*; Plenum Press: New York, 1970.

(12) Angell, C. A.; Imrie, C. T.; Ingram, M. D. From Simple Electrolyte Solutions Through Polymer Electrolytes to Superionic Rubbers: Some Fundamental Considerations. *Polym. Int.* **1998**, *47*, 9−15.

(13) Harris, K. R. Relations between the Fractional Stokes−Einstein and Nernst−Einstein Equations and Velocity Correlation Coefficients in Ionic Liquids and Molten Salts. *J. Phys. Chem. B* **2010**, *114*, 9572−9577.

(14) Xu, W.; Cooper, E. I.; Angell, C. A. Ionic Liquids: Ion Mobilities, Glass Temperatures, and Fragilities. *J. Phys. Chem. B* **2003**, *107*, 6170−6178.

(15) Angell, C. A.; Ansari, Y.; Zhao, Z. Ionic Liquids: Past, Present and Future. *Faraday Discuss.* **2012**, *154*, 9−27.

(16) Hansen, J.-P.; McDonald, I. R. *Theory of Simple Liquids*, 2nd ed.; Academic Press: London, 1986.

(17) Harrison, G. *The Dynamic Properties of Supercooled Liquids*; Academic Press: London, 1976.

(18) Ngai, K. L. Dynamic and Thermodynamic Properties of Glass-Forming Substances. *J. Non-Cryst. Solids* **2000**, *275*, 7−51.

(19) Zangi, R.; Kaufman, L. J. Frequency-Dependent Stokes−Einstein Relation in Supercooled Liquids. *Phys. Rev. E* **2007**, *75*, 051501.

(20) Kim, K.; Saito, S. Role of the Lifetime of Dynamical Heterogeneity in the Frequency-Dependent Stokes−Einstein Relation of Supercooled Liquids. *J. Phys. Soc. Jpn.* **2010**, *79*, 093601.

(21) Jarosz, G.; Mierzwa, M.; Ziozo, J.; Paluch, M.; Shirota, H.; Ngai, K. L. Glass Transition Dynamics of Room-Temperature Ionic Liquid 1-Methyl-3-trimethylsilylmethylimidazolium Tetrafluoroborate. *J. Phys. Chem. B* **2011**, *115*, 12709−12716.

(22) Sangoro, J. R.; Iacob, C.; Naumov, S.; Valiullin, R.; Rexhausen, H.; Hunger, J.; Buchner, R.; Strehmel, V.; Kärger, J.; Kremer, F. Diffusion in Ionic Liquids: The Interplay between Molecular Structure and Dynamics. *Soft Matter* **2011**, *7*, 1678−1681.

(23) Griffin, P. J.; Agapov, A. L.; Sokolov, A. P. Translation-Rotation Decoupling and Nonexponentiality in Room Temperature Ionic Liquids. *Phys. Rev. E* **2012**, *86*, 021508.

(24) Griffin, P. J.; Holt, A. P.; Wang, Y.; Novikov, V. N.; Joshua R. Sangoro, J. R.; Kremer, F.; Sokolov, A. P. Interplay Between Hydrophobic Aggregation and Charge Transport in the Ionic Liquid Methyltrioctylammonium Bis(trifluoromethylsulfonyl)imide. *J. Phys. Chem. B* **2014**, *118*, 783−790.

(25) Fukuda, M.; Terazima, M.; Kimura, Y. Sound Velocity Dispersion in Room Temperature Ionic Liquids Studied Using the Transient Grating Method. *J. Chem. Phys.* **2008**, *128*, 114508.

(26) Makino, W.; Kishikawa, R.; Mizoshiri, M.; Takeda, S.; Yao, M. Viscoelastic Properties of Room Temperature Ionic Liquids. *J. Chem. Phys.* **2008**, *129*, 104510.

(27) Yamaguchi, T.; Miyake, S.; Koda, S. Shear Relaxation of Imidazolium-Based Room-Temperature Ionic Liquids. *J. Phys. Chem. B* **2010**, *114*, 8126−8133.

(28) Shamim, N.; McKenna, G. B. Glass Dynamics and Anomalous Aging in a Family of Ionic Liquids above the Glass Transition Temperature. *J. Phys. Chem. B* **2010**, *114*, 15742−15752.

(29) Pogodina, N. V.; Nowak, M.; Läuger, J.; Klein, C. O.; Wilhelm, M.; Friedrich, Ch. Molecular dynamics of ionic liquids as probed by rheology. *J. Rheol.* **2011**, *55*, 241−256.

(30) Zorebski, E.; Geppert-Rybczyńska, M.; Zorebski, M. Acoustics as a Tool for Better Characterization of Ionic Liquids: A Comparative Study of 1-Alkyl-3-methylimidazolium Bis[(trifluoromethyl)sulfonyl]-imide Room-Temperature Ionic Liquids. *J. Phys. Chem. B* **2013**, *117*, 3867−3876.

(31) Šantić, A.; Wrobel, W.; Mutke, M.; Banhatti, R.; Funke, K. Frequency-Dependent Fluidity and Conductivity of an Ionic Liquid. *Phys. Chem. Chem. Phys.* **2009**, *11*, 5930−5934.

(32) Sangoro, J. R.; Kremer, F. Charge Transport and Glassy Dynamics in Ionic Liquids. *Acc. Chem. Res.* **2012**, *45*, 525−532.

(33) Yamaguchi, T.; Nakahara, E.; Sueda, K.; Koda, S. Interpretation of the Variation of Walden Product of Ionic Liquids with Different Alkyl Chain Lengths in Terms of Relaxation Spectra. *J. Phys. Chem. B* **2013**, *117*, 4121−4126.

(34) Wakai, C.; Oleinikova, A.; Ott, M.; Weingärtner, H. How Polar Are Ionic Liquids? Determination of the Static Dielectric Constant of an Imidazolium-Based Ionic Liquid by Microwave Dielectric Spectroscopy. *J. Phys. Chem. B* **2005**, *109*, 17028−17030.

(35) Weingärtner, H.; Sasisanker, P.; Daguenet, C.; Dyson, P. J.; Krossing, I.; Slattery, J. M.; Schubert, T. The Dielectric Response of Room-Temperature Ionic Liquids: Effect of Cation Variation. *J. Phys. Chem. B* **2007**, *111*, 4775−4780.

(36) Hunger, J.; Stoppa, A.; Schrödle, S.; Hefter, G.; Buchner, R. Temperature Dependence of the Dielectric Properties and Dynamics of Ionic Liquids. *ChemPhysChem* **2009**, *10*, 723−733.

(37) Turton, D. A.; Hunger, J.; Stoppa, A.; Hefter, G.; Thoman, A.; Walther, M.; Buchner, R.; Wynne, K. Dynamics of Imidazolium Ionic Liquids from a Combined Dielectric Relaxation and Optical Kerr Effect Study: Evidence for Mesoscopic Aggregation. *J. Am. Chem. Soc.* **2009**, *131*, 11140−11146.

(38) Buchner, R.; Hefter, G. Interactions and Dynamics in Electrolyte Solutions by Dielectric Spectroscopy. *Phys. Chem. Chem. Phys.* **2009**, *11*, 8984−8999.

(39) Nakamura, K.; Shikata, T. Systematic Dielectric and NMR Study of the Ionic Liquid 1-Alkyl-3-Methyl Imidazolium. *ChemPhysChem* **2010**, *11*, 285−294.

(40) Daschakraborty, S.; Biswas, R. Dielectric Relaxation in Ionic Liquids: Role of Ion-Ion and Ion-Dipole Interactions, And Effects of Heterogeneity. *J. Chem. Phys.* **2014**, *140*, 014504.

(41) Yamaguchi, T.; Koda, S. Mode-Coupling Theoretical Analysis of Transport and Relaxation Properties of Liquid Dimethylimidazolium Chloride. *J. Chem. Phys.* **2010**, *132*, 114502.

(42) Yamaguchi, T.; Koda, S. Assignment of the Dielectric Relaxation of Ionic Liquid and Its Implication to the Ionic Conduction Mechanism. *J. Mol. Liq.* **2011**, *164*, 49−52.

(43) Schröder, C. Collective Translational Motions and Cage Relaxations in Molecular Ionic Liquids. *J. Chem. Phys.* **2011**, *135*, 024502.

(44) Schröder, C.; Sonnleitner, T.; Buchner, R.; Steinhauser, O. The Influence of Polarizability on the Dielectric Spectrum of the Ionic Liquid 1-Ethyl-3-methylimidazolium Triflate. *Phys. Chem. Chem. Phys.* **2011**, *13*, 12240−12248.

(45) Kashyap, H. K.; Annapureddy, H. V. R.; Raineri, F. O.; Margulis, C. J. How Is Charge Transport Different in Ionic Liquids and Electrolyte Solutions? *J. Phys. Chem. B* **2011**, *115*, 13212−13221.

(46) Balucani, U.; Zoppi, M. *Dynamics of the Liquid State*; Oxford University Press: Oxford, U.K., 1994.

(47) Widegren, J. A.; Saurer, E. M.; Marsh, K. N.; Magee, J. W. Electrolytic Conductivity of Four Imidazolium-Based Room-Temperature Ionic Liquids and the Effect of a Water Impurity. *J. Chem. Thermodyn.* **2005**, *37*, 569−575.

(48) Behrends, R.; Kaatze, U. A High Frequency Shear Wave Impedance Spectrometer for Low Viscosity Liquids. *Meas. Sci. Technol.* **2001**, *12*, 519−524.

(49) Yamaguchi, T.; Hayakawa, M.; Matsuoka, T.; Koda, S. Electric and Mechanical Relaxations of Liclo$_4$-Propylene Carbonate Systems in 100 MHz Region. *J. Phys. Chem. B* **2009**, *113*, 11988−11998.

(50) Yamaguchi, T.; Yamada, Y.; Koda, S. Shear and Conductivity Relaxations of Lithium Ion Electrolytes in Polyethyleneglycol Dimethyl Ethers. *J. Mol. Liq.* **2012**, *172*, 93−101.

(51) Yamaguchi, T.; Mikawa, K.; Koda, S. Shear Relaxation of Water-Ionic Liquid Mixtures. *Bull. Chem. Soc. Jpn.* **2012**, *85*, 701−705.

(52) Buchner, R.; Hefter, G. T.; May, P. M. Dielectric Relaxation of Aqueous NaCl Solutions. *J. Phys. Chem. A* **1999**, *103*, 1−9.

(53) Yamaguchi, T.; Akatsuka, T.; Koda, S. Rheological Bases for Empirical Rules on Shear Viscosity of Lubrication Oils. *J. Phys. Chem. B* **2013**, *117*, 3232−3239.

(54) MacFarlane, D. R.; Forsyth, M.; Izgorodina, E. I.; Abbott, A. P.; Annat, G.; Fraser, K. On the Concept of Ionicity in Ionic Liquids. *Phys. Chem. Chem. Phys.* **2009**, *11*, 4962−4967.

(55) Schreiner, C.; Zugmann, S.; Hartl, R.; Gores, H. J. Fractional Walden Rule for Ionic Liquids: Examples from Recent Measurements and a Critique of the So-Called Ideal KCl Line for the Walden Plot. *J. Chem. Eng. Data* **2010**, *55*, 1784−1788.

(56) Del Pópolo, M. G.; Voth, G. A. On the Structure and Dynamics of Ionic Liquids. *J. Phys. Chem. B* **2004**, *108*, 1744−1752.

(57) Hu, Z.; Margulis, C. J. Room-Temperature Ionic Liquids: Slow Dynamics, Viscosity, and the Red Edge Effect. *Acc. Chem. Res.* **2007**, *40*, 1097−1105.

(58) Urahata, S. M.; Ribeiro, M. C. C. Unraveling Dynamical Heterogeneity in the Ionic Liquid 1-Butyl-3-methylimidazolium Chloride. *J. Phys. Chem. Lett.* **2010**, *1*, 1738−1742.

(59) Karimi-Varzaneh, H. A.; Müller-Plathe, F.; Balasubramanian, S.; Carbone, P. Studying Long-Time Dynamics of Imidazolium-Based Ionic Liquids with a Systematically Coarse-Grained Model. *Phys. Chem. Chem. Phys.* **2010**, *12*, 4714−4724.

(60) Andreussi, O.; Marzari, N. Transport Properties of Room-Temperature Ionic Liquids from Classical Molecular Dynamics. *J. Chem. Phys.* **2012**, *137*, 044508.

(61) Harris, K. R.; Kanakubo, M.; Tsuchihashi, N.; Ibuki, K.; Ueno, M. Effect of Pressure on the Transport Properties of Ionic Liquids: 1-Alkyl-3-methylimidazolium Salts. *J. Phys. Chem. B* **2008**, *112*, 9830−9840.

(62) Lopes, J. N. A. C.; Pádua, A. A. H. Nanostructural Organization in Ionic Liquids. *J. Phys. Chem. B* **2006**, *110*, 3330−3335.

(63) Russina, O.; Triolo, A. New Experimental Evidence Supporting the Mesoscopic Segregation Model in Room Temperature Ionic Liquids. *Faraday Discuss.* **2012**, *154*, 97−109.

(64) Fujii, K.; Kanzaki, R.; Takamuku, T.; Kameda, Y.; Kohara, S.; Kanakubo, M.; Shibayama, M.; Ishiguro, S.; Umebayashi, Y. Experimental Evidences for Molecular Origin of Low-Q Peak in Neutron/X-ray Scattering of 1-Alkyl-3-methylimidazolium Bis-(trifluoromethanesulfonyl)amide Ionic Liquids. *J. Chem. Phys.* **2011**, *135*, 244502.

(65) Shimizu, K.; Bernardes, C. E. S.; Lopes, J. N. C. Structure and Aggregation in the 1-Alkyl-3-Methylimidazolium Bis-(trifluoromethylsulfonyl)imide Ionic Liquid Homologous Series. *J. Phys. Chem. B* **2014**, *118*, 567−576.

(66) Rocha, M. A. A.; Neves, C. M. S. S.; Freire, M. G.; Russina, O.; Triolo, A.; Coutinho, J. A. P.; Santos, L. M. N. B. F. Alkylimidazolium Based Ionic Liquids: Impact of Cation Symmetry on Their Nanoscale Structural Organization. *J. Phys. Chem. B* **2013**, *117*, 10889−10897.

(67) Yamamuro, O.; Yamada, T.; Kofu, M.; Nakakoshi, M.; Nagao, M. Hierarchical Structure and Dynamics of an Ionic Liquid 1-Octyl-3-methylimidazolium Chloride. *J. Chem. Phys.* **2011**, *135*, 054508.

(68) Kofu, M.; Nagao, M.; Ueki, T.; Kitazawa, Y.; Nakamura, Y.; Sawamura, S.; Watanabe, M.; Yamamuro, O. Heterogeneous Slow Dynamics of Imidazolium-Based Ionic Liquids Studied by Neutron Spin Echo. *J. Phys. Chem. B* **2013**, *117*, 2773−2781.

(69) Yamaguchi, T.; Mikawa, K.; Koda, S.; Fujii, K.; Endo, H.; Shibayama, M.; Hamano, H.; Umebayashi, Y. Relationship between Mesoscale Dynamics and Shear Relaxation of Ionic Liquids with Long Alkyl Chain. *J. Chem. Phys.* **2012**, *137*, 104511.