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Quasielastic neutron scattering studies on glass-forming ionic liquids with imidazolium cations

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Relaxation processes for imidazolium-based ionic liquids (ILs) were investigated by means of an incoherent quasielastic neutron scattering technique. In order to clarify the cation and anion effects on the relaxation processes, ten samples were measured. For all of the samples, we found three relaxations at around 1 ps, 10 ps, and 100 ps-10 ns, each corresponding to the alkyl reorientation, the relaxation related to the imidazolium ring, and the ionic diffusion. The activation energy (E_a) for the alkyl relaxation is insensitive to both anion and alkyl chain lengths. On the other hand, for the imidazolium relaxation and the ionic diffusion processes, E_a increases as the anion size decreases but is almost independent of the alkyl chain length. This indicates that the ionic diffusion and imidazolium ring) and the anions. This is consistent with the fact that the imidazolium-based ILs have nanometer scale structures consisting of ionic and neutral (alkyl chain) domains. It is also found that there is a clear correlation between the ionic diffusion and viscosity, indicating that the ionic diffusion is mainly associated with the glass transition which is one of the characteristics of imidazolium-based ILs. (0.2015 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4937413]

I. INTRODUCTION

In the past decade, ionic liquids (ILs) have become a topic of increasing attention in many fields, since they possess several unique properties, such as negligible vapor pressure, non-flammability, high ionic conductivity, and wide range of solubility. It is also notable that their physicochemical properties are controlled by varying cations and anions, making ILs versatile for various applications. The ILs are usually composed of bulky and asymmetric organic cations and common anions. The cation of ILs has a core part with a positive charge and a neutral alkyl chain. Although a wide range of anions are typically explored, ranging from halogens to inorganic/organic ionic groups, a common cation typically used is 1-alkyl-3-methylimidazolium ions which are investigated in this work. They are often abbreviated as CnmimX, where n is the alkyl-carbon number and X is the anion. The chemical structures of the cations and anions investigated in this work are shown in Fig. 1.

So far, a large number of X-ray/neutron scattering¹⁻¹⁸ and computer simulation studies^{12,19-24} have been performed to clarify the structure of C*n*mimX. One of the central issues in the imidazolium-based ILs is the origin of the peak which appears at a low scattering vector ($Q = 0.2-0.3 \text{ Å}^{-1}$). The low-Q peak corresponds to the distance between two polar entities (core parts of cations or anions) separated

by non-polar entities (alkyl chains of cations). However, the three-dimensional arrangement of the ions and alkyl chains (nanostructure) is not fully understood. To address this issue, we have recently investigated the phase behavior and structure of CnmimPF₆ (n = 4-16) and CnmimCl (n = 4-14) by means of differential scanning calorimetry (DSC) and X-ray diffraction (XRD) techniques.²⁵ It is known that the PF_6 samples with n > 13 and the Cl samples with n > 10 exhibit smectic A liquid-crystalline (LC) to liquid (L) phase transitions.^{26–32} We found that the LC phase exists in supercooled (metastable) states even for the samples with n < 10. Furthermore, the XRD patterns of these samples demonstrated the evident similarity between the low-Q peaks in the L phase and the diffraction peaks in the LC phase. Therefore, it is concluded that the nanostructure of CnmimX is essentially the same as the layered structures in the LC phases though the degree of ordering is totally different. Recent molecular dynamics (MD) simulation works also support our conclusion.^{33,34}

Dynamical properties of *Cn*mimX have also been investigated by means of several techniques, such as nuclear magnetic resonance (NMR),^{15,35–44} quasielastic neutron scattering (QENS),^{11,16,45–51} viscoelastic,^{37,38,40,50,52–55} dielectric,^{41,56–59} and ionic conductivity^{37,38,40,60–63} measurements. The unique feature of QENS is that it probes the diffusion process at atomistic scales of space (1–100 Å) and time (1 ps–10 ns) simultaneously. Another feature of QENS is that either incoherent or coherent scattering can be dominant by selective deuteration; $\sigma_{coh}(H) = 1.76$ b, $\sigma_{inc}(H) = 80.27$ b,

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(a) cations



FIG. 1. Schematic structures and abbreviations of (a) cations and (b) anions of ionic liquids investigated in this work.

 $\sigma_{\rm coh}({\rm D}) = 5.59$ b, and $\sigma_{\rm inc}({\rm H}) = 2.05$ b, where σ is a neutron scattering cross section and b(barn) is equal to 10^{-24} cm². For hydrogenated materials having large incoherent scattering cross section due to H atoms, the self-diffusion process can be examined. On the other hand, in deuterated ones in which the coherent scattering is dominant, one can obtain the information on the collective dynamics.

The incoherent QENS studies were reported for C4mimPF₆,^{45,46} C4mimCl,⁴⁷ and C*n*mimBr.^{49,51} Several diffusion processes including translational diffusion and local motions were found in these works. The collective dynamics was investigated for several deuterated C*n*mimX with relatively long alkyl chains (n = 6-12) by using neutron spin echo (NSE) technique.^{11,16,48,50} In these papers, the correlation between the translational diffusion and the viscosity is also discussed. In d-C8mimX (X = Cl, PF₆, TFSI),^{11,16} we have succeeded to observe the hierarchical dynamics, that is the relaxation of nanostructure, the ionic diffusion, and the alkyl chain dynamics, by choosing the

scattering vector Q corresponding to the specific correlation. Recently, not only C*n*mimX but also pyridinium-based ILs have been investigated by the incoherent and coherent QENS techniques.^{64,65}

Despite the QENS works mentioned above, only fragmentary information on the dynamics is available at present. Moreover, the previous QENS results are sometimes in conflict with each other. This may be because the results strongly depend on analytical models in the case where multiple motions exist. To overcome this difficulty, it is necessary to investigate the dynamics in a wide time region. Furthermore, systematic studies with changing anions/cations are important to characterize the dynamics of CnmimX.

In this article, we report our incoherent QENS work for the 10 samples of C*n*mimX (n = 2, 4, 8 and X = Cl, I, NO₃, PF₆, TF, FSI, TFSI). Here, only cations involve hydrogen atoms, so that the motion of the cations is "visible" in these measurements. In order to explore the dynamics in a wide time range, two spectrometers with different energy resolutions and windows were used. We aim at investigating (i) the overall feature of the dynamics of *Cn*mimX and (ii) how the relaxation processes are influenced by changing anions or cations. Our goal is to understand what governs the hierarchical dynamics in *Cn*mimX.

Another interest is the relation between the microscopic dynamics investigated by QENS and the glass transition which is one of the characteristics of imidazolium-based ILs. Which dynamical process is mainly related to the glass transition? In fact, a large jump in heat capacity at the glass transition temperature (T_g) predominantly comes from the freezing of the configurational motions of the alkyl chain.^{11,66–69} This result may suggest that the alkyl dynamics is significant for the glass transition. However, T_{g} depends on the anion species but little on the alkyl chain length, indicating that the ionic interaction governs the glass transition. The nanostructure also might be associated with the glass transition as in the case of cooperatively rearranging regions (CRRs) of the molecular glass-forming liquids. To make clearer comparison, we have also measured the viscosities, which are directly related to the glass transitions, of some of the same samples used in the QENS experiments.

II. EXPERIMENTAL

A. Samples

The samples of *Cn*minI (n = 3, 4, 6) were provided by Professor Nakakoshi in Yokohama National University. All other samples were purchased from commercial sources; C4mimNO₃ from J & K Chemical Ltd., C4mimX (X = Cl, PF₆, FSI, TFSI) from Kanto Chemical Co., Inc., and C2mimTFSI, C4mimTF, and C8mimX (X = Cl, PF₆, TFSI) from Ionic Liquids Technologies GmbH. The nominal purities of the samples were specified as >99%. The samples with Cl were dried under vacuum (1 Pa) above 80 °C for a few hours. Other samples were used without further purification.

B. Quasielastic neutron scattering

The QENS experiments were performed using two instruments, the time-of-flight chopper spectrometer AGNES,⁷⁰ which is owned by ISSP, University of Tokyo and located at the research reactor JRR-3 in Japan Atomic Energy Agency, and the backscattering spectrometer HFBS⁷¹ at the NIST Center for Neutron Research in USA. The incident neutron energy used was 4.6 meV at AGNES, giving rise to energy resolutions (full width at half-maximum of the elastic peak) of $\Delta E = 0.12$ meV. The accessible energy window and Q-range were $-4 \text{ meV} < \hbar\omega < 20 \text{ meV}$ and $0.26 \text{ Å}^{-1} < Q < 2.7 \text{ Å}^{-1}$, respectively. While, in the experiments on HFBS, the final neutron energy was fixed to 2.08 meV. The energy resolution, energy window, and Q-range were $\Delta E = 0.8 \ \mu eV$, $-17 \ \mu eV$ $<\hbar\omega$ < 17 µeV, and 0.25 Å⁻¹ < Q < 1.75 Å⁻¹, respectively. The raw data were reduced using an in-house software at AGNES and the DAVE software package⁷² at HFBS.

The samples were loaded into concentric double-cylinder Al cans with He gas, which facilitates thermal equilibration inside the cans. The thickness of the sample confined between the two Al walls was 0.2-0.5 mm, giving a neutron transmission of 85%-90%, in order to reduce multiple scattering effects. The temperature of the samples was controlled by placing them in top-loading closed cycle refrigerators. The QENS measurements were carried out at temperatures between 280 K and 360 K on AGNES and between 240 K and 400 K on HFBS. The resolution data were taken at 20 K or 100 K on AGNES and 10 K on HFBS.

C. Viscosity

Viscosities of C8mimX (X = Cl, PF₆, TFSI) and C4mimFSI were measured by a Bohlin Gemini II rotational rheometer. A liquid nitrogen or electronic Peltier cooling systems was used depending on the temperature range of the measurements. As for C8mimX, in order to measure the viscosity in a wide temperature range, typically between 210 K and 295 K, a parallel plate geometry was chosen. The plate diameter was 25 mm and the gap between the plates was set to 1 mm. The viscosity of C4mimFSI was measured at 10 °C using a cone and plate geometry with the diameter of 40 mm and the conical angle of 4°. For all of the samples, the complex viscosity was evaluated in an oscillatory mode at the constant strain amplitude (1%) and the frequency (1 Hz).

III. RESULTS AND DISCUSSION

A. Quasielastic neutron scattering

Figure 2 shows, as an example, the observed dynamical structure factor of C8mimTFSI at $Q = 1.7 \text{ Å}^{-1}$ and T = 300 K, taken on the AGNES spectrometer. Solid curves represent the results of the fitting with the functions described below as

$$S(Q,\omega) = R(Q,\omega) \otimes [A_{\rm E}(Q)\delta(\omega) + A_1(Q)L_1(\omega) + A_2(Q)L_2(\omega)] + {\rm BG},$$
(1)

$$L_i(\omega) = \frac{1}{\pi} \frac{\Gamma_i}{\omega^2 + \Gamma_i^2},\tag{2}$$

where $R(Q,\omega)$ is the resolution function of the AGNES spectrometer, $\delta(\omega)$ is the delta function, $L_1(Q,\omega)$ and $L_2(Q,\omega)$ are Lorentz functions, \otimes represents the operator of the



FIG. 2. Dynamic structure factor of C8mimTFSI observed at $Q = 1.7 \text{ Å}^{-1}$ and T = 300 K. The data are taken on the AGNES instrument. The curves are the results of the fitting. See the text for details.

convolution, and BG is a linear background. $A_{\rm E}(Q)$, $A_1(Q)$, and $A_2(Q)$ display the areas of elastic, wider Lorentzian, and narrower one, respectively. The fitting was satisfactory as shown in Fig. 2. The fitting procedures for all datasets were carried out by using the PAN program in the DAVE software package.⁷²

In order to inquire into the origins of two relaxation processes, the *Q*-dependence of the peak width (Γ) and EISF (Elastic Incoherent Structure Factor) for each relaxation are plotted in Fig. 3. Both Γ_1 and Γ_2 exhibit little change in *Q*, suggesting that the relaxation processes are of local origin. The relaxation times for the faster and slower motions are around 1 ps and 10 ps, respectively, by considering that the relaxation time (τ) is inversely proportional to Γ . The *Q*-dependence of EISF is indicative of the geometry of intramolecular motions and the number of H atoms which contributes to each QENS component. The EISF_i is defined as

$$EISF_{1} = \frac{A_{E} + A_{1}}{A_{E} + A_{1} + A_{2}},$$

$$EISF_{2} = \frac{A_{E}}{A_{E} + A_{2}},$$
(3)

where $EISF_1$ is for the faster relaxation, while $EISF_2$ is for the slower one.

The dashed curve in Fig. 3(b) is the calculated EISF assuming the rotation of methyl groups (three-fold jump). This model is considered first since the methyl rotation is often the fastest motion in organic systems. There are two methyl groups in the cation of C8mimTFSI; one is at the end of the alkyl chain and the other attached to the imidazolium ring. Since only 6 out of 23 hydrogen atoms contribute to the motion, the EISF is written as⁷³

EISF(CH₃ rot.) =
$$\frac{17}{23} + \frac{6}{23}\frac{1}{3}\left[1 + 2j_0\left(\sqrt{\frac{8}{3}}Qd\right)\right],$$
 (4)

where d (= 1.09 Å) is the distance between the hydrogen and carbon atoms, and j_0 is the spherical Bessel function of zeroth order. As can be seen, this model cannot explain the experimental EISF₁. The actual value of EISF₁ is much smaller than 17/23, indicating that a large number of hydrogen atoms contribute to the faster relaxation.

Now we consider the dynamical model where the hydrogen atoms in the alkyl and the methyl groups rotate on a circle of radius *R*. The EISF for a random jump model among *N* equivalent sites on a circle, which is equivalent to the continuous rotational diffusion model in the limit $N \rightarrow \infty$,



FIG. 3. *Q*-dependence of (a) Γ_1 , (b) Γ_2 , (c) EISF₁, and (d) EISF₂ for C8mimTFSI, taken on AGNES. The dashed and solid curves in (b) and (d) are the EISF calculated for the dynamical model described in the text. Error bars throughout the text represent one standard deviation.

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is described as follows:^{73,74}

EISF(circ. rot.) =
$$\frac{3}{23} + \frac{20}{23} \frac{1}{N} \sum_{n=1}^{N} j_0 \left[2QR \sin\left(\frac{n\pi}{N}\right) \right].$$
 (5)

Here, we assume that the three hydrogen atoms in the imidazolium ring are immobile. The calculated EISF with R = 1.2 Å and N = 100 is shown as the solid curve in Fig. 3(b). It should be noted that the model for large $N \ (N \ge 6)$ gives practically the same result in this Q-range. This model reasonably reproduces the actual EISF₁ at high temperature. The radius of 1.2 Å is larger than the radius of gyration (0.76 Å) for the alkyl chains keeping the all-trans conformation. This indicates that the rotation of the alkyl chains is more random and occupying wider space. Actually, the hydrogen atoms far from the imidazolium ring move faster around a wider space, while those near the ring move slower in a restricted space. It should be noted that the relaxation times and the radius R are "averaged" values for the complicated motions of alkyl chains mentioned above. Upon cooling, EISF₁ tends to increase, reflecting that the number of mobile hydrogen atoms decreases at low temperature. Though our model is oversimplified, it can be concluded that the faster relaxation is assigned to the intramolecular rotation of the alkyl chains.

The EISF₂ exhibits a minimum at $Q \sim 2$ Å⁻¹. The contribution from the faster relaxation (A_1) is omitted in Eq. (3), so that only the slower relaxation is considered in EISF₂. As discussed above, 17 hydrogen atoms in the alkyl and the methyl groups attribute to the faster relaxation. So the slower relaxation should originate from a motion of 3 hydrogen atoms in the imidazolium ring. To describe the EISF₂, we tested the restricted diffusion model where a particle diffuses within a sphere of radius r,^{73,75}

EISF(restricted) =
$$(1 - A) + A \left[\frac{3j_1(Qr)}{Qr}\right]^2$$
, (6)

where j_1 is the spherical Bessel function of first order. The solid curve in Fig. 3(d) represents the calculated EISF with r = 1.7 Å and A = 0.92. The small constant term (1 - A = 0.08) is probably due to a coherent contribution and/or some background. It should be pointed out that the radius of sphere is smaller than the distance between the center of the imidazolium ring and the hydrogen atom in the ring (2.25 Å). The slower relaxation does not correspond to an overall rotation of the ring but a librational relaxation in the restricted area.

As for other ILs measured, similar Q-dependence of Γ_i and EISF_i is observed. The feature of two relaxation processes is common in the imidazolium-based ILs. The temperature dependence of the relaxation times and their activation energies are shown and discussed in Sec. III B.

In order to explore a relaxation in the time scale of ns, QENS measurements were carried out using the high-resolution instrument HFBS. Figure 4 contains a representative set of data recorded at T = 300 K as a function of Q for C8mimTFSI. Here, we show both the dynamic structure factor $S(Q,\omega)$ in the frequency domain and the intermediate scattering function I(Q,t)/I(Q,0) in the time



FIG. 4. (a) Dynamic structure factors and (b) intermediate scattering functions of C8mimTFSI observed at T = 300 K. Colors of symbols correspond to different *Q*s. The data are taken on the HFBS instrument. The curves are the results of the fitting. See the text for details.

domain. The I(Q,t)/I(Q,0) was obtained as the Fourier transform of $S(Q,\omega)$ by using the fast Fourier transform algorithm in the DAVE package. In both $S(Q,\omega)$ and I(Q,t)/I(Q,0), a clear relaxational behavior was observed. As Q is increased, the spectrum becomes broader in $S(Q,\omega)$ and the I(Q,t)/I(Q,0) relaxes in a shorter time. It indicates that the relaxation time depends on Q, unlike in the case of the local relaxation processes as shown above.

The I(Q,t)/I(Q,0) data were fitted with the Kohlrausch-Williams-Watts (KWW) stretched exponential function,

$$\frac{I(Q,t)}{I(Q,0)} = (1-B) + B \exp\left\{-(t/\tau_3)^{\beta}\right\},\tag{7}$$

where *B* is a prefactor and β a stretching parameter accounting for the deviations from the simple exponential behavior. Since there is no analytical transform of the KWW function in the frequency domain (except for $\beta = 0.5$), the data are fitted in the time domain in the usual analysis. The prefactor *B* decreases at higher *Q* and higher *T*. This results from the presence of the relaxation processes faster than 0.1 ns, that is two local motions observed in the measurements on AGNES. As for the parameter β , the obtained values are 0.5-0.6 for all of the samples. As seen in Fig. 4(b), the fits were satisfactory. We tested to reproduce the curves in Fig. 4(a) by the Fourier



FIG. 5. *Q*-dependence of the inverse of the relaxation times $\langle \tau_3 \rangle$ obtained from the HFBS data of C8mimTFSI taken at *T* = 300 K. See the text for details.

transform of the KWW function with the parameters τ and β determined by the fitting and an adjustable scale factor. The results are satisfactory as shown by the solid curves in Fig. 4(a).

In Fig. 5, we show the inverse of the relaxation time $\langle \tau_3 \rangle$ obtained from the fitting analysis as a function of Q. Here, the average relaxation time is evaluated using the relation $\langle \tau \rangle = \tau/\beta \cdot \Gamma(1/\beta)$ (Γ is the gamma function). The $\langle \tau_3 \rangle^{-1}$ increases with an increase in Q, indicating that the relaxation is not a local motion but a translational diffusion process. The Q-dependence of $\langle \tau_3 \rangle^{-1}$ can be reproduced well by a jump diffusion model,^{73,76}

$$\langle \tau(Q) \rangle^{-1} = \frac{DQ^2}{1 + DQ^2 \tau_{\rm r}},\tag{8}$$

where the diffusion coefficient *D* and the residence time τ_r were estimated to be 3.1×10^{-11} m² s⁻¹ and 5.7×10^{-11} s, respectively, for C8mimTFSI at 300 K. The obtained *D* value is close to the literature values (~ 1.3×10^{-11} m² s⁻¹) by Pulsed Field Gradient Nuclear Magnetic Resonance (PFG NMR) measurements.^{38,42} Thus, the relaxation observed on HFBS is assigned to be the ionic diffusion (to be exact the diffusion of cations in the incoherent QENS measurements).

B. Temperature dependence of relaxation times

The temperature dependence of the relaxation times obtained from our QENS measurements is plotted in Fig. 6. As mentioned in Sec. III A, three types of relaxation processes are identified: (i) the relaxation related to the alkyl/methyl groups, (ii) the relaxation related to the imidazolium ring, and (iii) the ionic diffusion. Figures 6(a) and 6(b) display the Arrhenius plots for the relaxations (i) and (ii) for C4mimX and C*n*mimTFSI, respectively. Similarly, Figures 6(c) and 6(d) represent anion and alkyl carbon number dependences of the relaxation (iii) at $Q = 1 \text{ Å}^{-1}$. It is obvious that τ_1 depends on neither anions nor cations (alkyl carbon number). On the other hand, τ_2 and $\langle \tau_3 \rangle$ are sensitive to the anion species but are less influenced by the alkyl chain length.

In order to estimate activation energies (E_a) of the three relaxation processes, the temperature dependence of the relaxation times are fitted with the Arrhenius equation $\tau = \tau_0 \exp(E_a/k_BT)$. The obtained E_a values are plotted against anion radius (r_{anion}) and alkyl carbon number (n) in Fig. 7. The $r_{\rm anion}$ value used here is the ionic radius given by Goldschmidt for anionic halogen, the value of the thermochemical radius for PF₆ and NO₃,⁷⁷ and the value calculated from the van der Waals volume for other anions.⁷⁸ There is a clear tendency that E_a of τ_2 and $\langle \tau_3 \rangle$ decreases as r_{anion} increases. However both of them are little affected by the alkyl chain length. It is evident that the ionic diffusion $(\langle \tau_3 \rangle)$ and the relaxation related to the imidazolium ring (τ_2) are governed by the coulombic interaction between the core parts of the cations (imidazolium ring) and the anions; their E_a become higher for the smaller anions providing stronger coulombic interaction. In regard to τ_1 , E_a remains almost unchanged by r_{anion} and n.

These observations can be understood in terms of the nanoscale segregation in *Cn*mimX. Since the polar domains are separated by the nonpolar (alkyl chain) domains, the ionic diffusion ($\langle \tau_3 \rangle$) and the relaxation of the imidazolium ring (τ_2) occur independently of the length of the alkyl chain. Conversely, the ionic interaction causes no change in the motion of the alkyl chain (τ_1) which is controlled by the local potential surface subject to the configuration of the neighboring CH₂ groups.

Now we have obtained all of the QENS data to build the overall relaxation map of CnmimX. Figure 8 shows the relaxation map of C8mimTFSI at $Q = 1 \text{ Å}^{-1}$. Let us overview our QENS results. The reorientation of the alkyl/methyl group takes place on a time scale of 1 ps and exhibits a weak temperature dependence ($E_a \sim 5 \text{ kJ mol}^{-1}$). We found another local relaxation process, the rotational relaxation of the imidazolium ring in the restricted area, at 1-10 ps region, having a larger E_a (15–25 kJ mol⁻¹). The ionic diffusion occurs on a time scale of 0.1-10 ns. The E_a of the process $(30-50 \text{ kJ mol}^{-1})$ is larger than those of the above two local processes and strongly depends on the anion species. For the ILs with longer alkyl chain (n > 4), the diffraction peak is clearly observed at $Q = 0.2-0.3 \text{ Å}^{-1}$, which corresponds to the layer spacing (~ 2 nm) of the lamellar structure, as introduced in Sec. I. The relaxation related to the nanostructure was investigated in the previous study using the NSE instrument.¹⁶ The relaxation data of d-C8mimTFSI taken at $Q = 0.3 \text{ Å}^{-1}$ are also shown in Fig. 8. The relaxation time of the nanostructure relaxation is slower than that of the ionic diffusion but its temperature dependency is similar to that of the ionic diffusion in this temperature range. This indicates that the nanoscale structure is also mainly governed by the Coulomb interaction, as discussed in the previous paper.¹⁶ On further cooling toward $T_{\rm g}$ or with increasing the alkyl chain length, the nanostructure grows and the related activation energy may become larger than that of the ionic diffusion. Further experiment with a high-spec NSE instrument is required to explore this point.

C. Comparison with viscosity

It is of interest to compare the relaxation times obtained by the QENS measurements with viscosities. Figure 9 shows the Arrhenius plots of $\langle \tau_3 \rangle$ (left axis) and viscosity (right axis) for C8mimX (X = Cl, PF₆, TFSI). We have chosen C8mimX because their supercooled liquid phases are stable. The interrelation between the scales of $\langle \tau_3 \rangle$ and η is determined as described in the next paragraph. Interestingly, for all samples examined, both $\langle \tau_3 \rangle$ and η data sets lie on a single curve. This suggests that the ionic diffusion detected in the QENS measurements corresponds to the " α -process" in the language of glass physics. The α -process, which is directly related to viscosity, slows down upon cooling and its relaxation time reaches 10^2-10^3 s at T_g .

The Arrhenius plot as a function of reduced temperature T_g/T , or the so-called "Angell plot," is discussed frequently for glass-forming liquids.^{79,80} Figure 10 shows the Angell plot for $\langle \tau_3 \rangle$ and viscosity. The scales for the relaxation time and viscosity were adjusted as is in the usual Angell plot but slightly shifted in respect to the left axis. This is because the relaxation time of the diffusion process changes with Q. The same adjustment was made also for Fig. 9. Angell introduced the fragility m, which characterizes how rapidly the dynamics slows down toward T_g .^{79,80} The fragility index m is defined as

$$m = \left. \frac{d(\log \tau)}{d(T_{\rm g}/T)} \right|_{T=T_{\rm g}}.$$
(9)

In order to determine the fragility of C8mimX, we fit the experimental viscosity and QENS data to the Vogel-Fulcher-Tamman equation,^{81–83}

$$\eta = \eta_0 \exp\left(\frac{D}{T - T_0}\right),\tag{10}$$

where η_0 is the infinite high temperature viscosity, T_0 the Vogel temperature, and D is a parameter controlling the curvature. We imposed a constraint, $\eta(T_g) = 10^{12}$ Pa s, and then the fragility *m* is rewritten as

$$m = \frac{D}{\ln 10} \frac{T_{\rm g}}{(T_{\rm g} - T_0)^2} = (12 - \log \eta_0) \frac{T_{\rm g}}{(T_{\rm g} - T_0)}.$$
 (11)

The obtained *m* values are 72.9 for Cl, 88.5 for PF₆, and 157.6 for TFSI. The larger the anion is, the higher *m* becomes. Since the viscosities of C8mimX were measured in the limited temperature range, the fragility index depends on the choice of the limit values at $T \rightarrow T_g$ and $T \rightarrow \infty$. Therefore, the



FIG. 6. Arrhenius plots of relaxation times of the faster (τ_1) and slower (τ_2) local processes observed on AGNES and the ionic diffusion ((τ_3)) at Q = 1.0 Å⁻¹ on HFBS. The upper panels (a) and (c) display anion dependence of the relaxation times for *Cn*mimX with the common C4mim cation. The lower panels (b) and (d) show the alkyl carbon number dependence for *Cn*mimX with common TFSI anion. Solid lines represent the results of the fit with assuming the Arrhenius law.



FIG. 7. Activation energies against (a) anion radius (r_{anion}) and (b) alkyl carbon number (n).

fragility indices we obtained are somewhat different from those previously reported, 54,61,62 but similar anion dependence was seen, i.e., the *m* value slightly decreases with increasing alkyl-chain length, ⁶¹ while it is significantly influenced by the type of anion. ⁶²



FIG. 8. Overall relaxation map of C8mimTFSI. The slowest relaxation (nanostructure relaxation) are the data from the NSE measurements for d-C8mimTFSI.¹⁶ Solid curves are the guides to the eye.

Finally, we present a correlation plot between the relaxation times $\langle \tau_3 \rangle$ and viscosities at 10 °C in Fig. 11. All of the samples measured in the present QENS work are contained. The viscosity data of the samples except C8mimX and C4mimFSI are taken from the literatures.^{37,52} The $\langle \tau_3 \rangle$ has a linear relationship with η as is evident in the plot. It also demonstrates that the ionic diffusion mainly governs the viscosity directly related to the glass transition. A question may arise as to whether or not the nanostructure affects the viscosity. Recently, we found that the glass transition occurs in both the smectic A liquid crystalline and the supercooled liquids phases of C9.5mimPF₆ and their T_g 's



FIG. 9. Arrhenius plots of the relaxation times $\langle \tau_3 \rangle$ and viscosity for C8mimX (X = Cl, PF₆, TFSI). Vertical dashed lines represent the glass transition temperature for each sample. Open triangles show the viscosity data reported earlier.⁵²

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FIG. 10. Arrhenius plots of the relaxation times $\langle \tau_3 \rangle$ and viscosity as a function of the reduced temperature T_g/T for C8mimX (X = Cl, PF₆, TFSI). Open triangles show the viscosity data reported earlier.⁵²



FIG. 11. Correlation plot between the relaxation times of the ionic diffusion $\langle \tau_3 \rangle$ and viscosities at 10 °C. The viscosities of the samples except C8mimX and C4mimFSI are taken from the literatures.^{37,52}

are almost the same.²⁵ It suggests that the characteristic length of the glass transition, which may correspond to CRR,⁶⁷ is smaller than the size of the layer structure (nanostructure). This result also supports our conclusion. For ILs with longer alkyl chains, however, it is possible that the nanostructure affects the viscosity. Actually, there is a report suggesting that the viscosity tends to increase with the development of the nanostructure for ILs with $n > 10.^{84}$

IV. CONCLUSIONS

We have investigated microscopic dynamics of imidazolium-based ionic liquids (CnmimX) by using an

incoherent QNES technique. In order to clarify how the microscopic dynamics is affected by changing the anion species and alkyl chain length and what governs the dynamics, ten samples of CnmimX (n = 2, 4, 8 and X = Cl, I, NO₃, PF₆, TF, FSI, TFSI) were measured. In all of the samples, three relaxation processes exist in the time scale of the present measurement (0.1 ps-10 ns). The alkyl reorientation with the time scale of ca. 1 ps depends on neither the anion species nor the alkyl chain length. The relaxation process at ca. 10 ps is assigned to the relaxation related to the imidazolium ring, probably a librational relaxation in the restricted area. This process weakly depends on the anion and insensitive to the alkyl chain length. The relaxation time of the slowest process (100 ps-10 ns) changes with the scattering vector Q in contrast to the above faster processes. Its Q-dependence was reproduced well by a jump diffusion model. We thus assign it to the ionic diffusion process. The activation energy of the ionic diffusion increases with decreasing the anion size but remains almost unchanged with the alkyl chain length. It is evident that the ionic diffusion and the imidazolium relaxation are governed by the Coulombic interaction between the core parts of cations (imidazolium ring) and anions. Furthermore, the fact that all of the relaxation processes are less influenced by the alkyl chain length should be related to the existence of the nanoscale segregation of polar/nonpolar entities in CnmimX. Combining the present and previous QENS data, we have made the overall relaxation map of CnmimX for the first time.

In order to reveal the relationship between the microscopic dynamics and the glass transition in CnmimX, viscosities of some of the same samples as in the QENS experiments were also measured. It is found that the fragility index increases in the order [CI] < [PF₆] < [TFSI]. We have also demonstrated that the relaxation times of the ionic diffusion has a linear relationship with the viscosity for all of the samples used in this work. This suggests that Coulombic interaction governs the ionic diffusion, viscosity, and the glass transition. We did not find the strong correlation between the viscosity and the existence of the nanostructure in this work.

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Certain commercial equipment, instruments, or materials are identified in this paper to foster understanding. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

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