

Frequency-Domain Investigation of the Ionic Mobility of Triflate Salts in Tetrahydrofuran

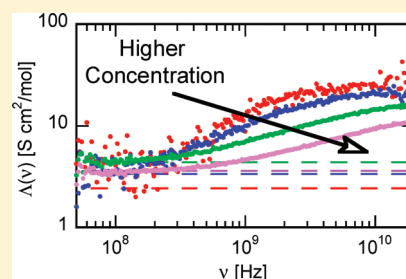
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ABSTRACT: The frequency-dependent molar conductivities of two triflate salts, tetrabutylammonium triflate (TBATf) and lithium triflate (LiTf), in tetrahydrofuran are measured in the microwave frequency domain at the concentrations where the direct-current molar conductivity increases with concentration. The relaxation frequency of the conductivity of TBATf increases with concentration as was demonstrated by a simulation and theoretical calculation on a simple model system. However, the low-frequency side of the relaxation of the conductivity of LiTf grows with increasing concentration, suggesting the presence of large aggregates such as triple ions. The molar conductivities of both salts at 20 GHz are about an order of magnitude smaller than those predicted by the Nernst–Einstein relationship, indicating the importance of the picosecond or faster dynamics in the determination of the absolute value of the conductivity.



1. INTRODUCTION

The molar conductivity of an electrolyte solution is usually a decreasing function of the concentration of salt in solvents of high dielectric constant, reflecting the stronger effects of inter-ionic interactions. However, the increase in the molar conductivity with concentration is often observed in solvents of low polarity at the intermediate concentration regime, leading to the presence of the molar conductivity minimum.^{1–10}

In addition to its scientific interest, the molar conductivity minimum possesses a practical importance for the development of lithium ion secondary batteries because it is often observed in the molar conductivity of lithium salts in organic solvents of low polarity designed for the electrolytes of higher safety. For example, the molar conductivity minimum is found in polyethylene oxide-based polymer electrolytes, which is a candidate as a solid electrolyte.^{11–17} Since the mechanism of the molar conductivity minimum is involved in the ionic conduction of these systems, its understanding is indispensable for the clarification of the conduction mechanism.

The decrease in molar conductivity with concentration below the minimum is naturally understood in terms of the increase in the effects of interionic interactions, and what requires special explanations is the increase in molar conductivity above the minimum. The increase in molar conductivity has traditionally been elucidated by ionic association models. Roughly speaking, there are two different association models for the increase in molar conductivity, namely, the triple ion and redissociation models. The former ascribes the increase in the molar conductivity to the formation of charged triple ions from the neutral ion pairs^{1,2,18,19} and the latter to the redissociation of ion pairs into free ions.³

Both models approximate the ionic conduction as the superposition of the nearly isolated motions of ionic clusters, and the concentration dependence of the molar conductivity is attributed to the change in the population ratio of the clusters.

We recently performed a Brownian dynamics simulation on the simplest model system on which the two association models are based in order to clarify the general behavior of ionic transports as a function of the concentration of salts and the polarity of solvents.²⁰ Although the simulation disagrees with real electrolyte solutions in some characteristics, it succeeded in reproducing the presence of the molar conductivity minimum when the polarity of solvent is sufficiently low. Surprisingly enough, however, neither of the static association models can describe the simulation results. The mechanism suggested by the simulation is different from those of static association models in that it accompanies the decrease in the relaxation time of conductivity with increasing the concentration of ions. Our theoretical analysis of the simulation shows that the relaxation observed in the simulation is due to the collective dynamics of ions, which reduces to the relaxation of the ionic atmosphere in the low concentration regime.²¹ Since the relaxation of the conductivity can be measured experimentally in the frequency domain, we can examine by experiment whether the mechanism suggested by the simulation is present in real systems.

In this work, we apply microwave dielectric spectroscopy to electrolyte solutions that show molar conductivity minima. The frequency-dependent conductivity can be determined by dielectric

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spectroscopy with relative ease, and the measurement of the frequency-dispersion of the conductivity is a powerful tool to investigate the conduction mechanisms of solid state electrolytes and supercooled ionic liquids.²² The frequency-dependent conductivity tells us the time scale of the dynamics of ions from which we can extract the information on microscopic processes involved in ionic conduction. Surprisingly, however, the number of applications of the dielectric spectroscopy to the molar conductivity minimum is rather limited to our best knowledge.^{23–25}

The systems we investigate here are the solutions of triflate (trifluoromethanesulfonate, CF_3SO_3^- , denoted as Tf^-) salts in tetrahydrofuran (THF), whose dielectric constant is 7.6 at 25 °C.²⁶ The cations are lithium and tetrabutylammonium (TBA), whose ionic sizes are quite different from each other. The solutions of both salts in THF were reported to show minima of molar conductivity in THF.^{5,6,8} Vibrational spectroscopy has also been applied to these salts in solvents of low polarity in order to investigate the ionic association. LiTf clearly shows a band assigned to the ion pair, and the presence of the triple ions in the spectroscopic sense is also suggested.^{8,27} However, TBATf shows no vibrational band ascribed to the ion pair.⁷ Provided the difference in the sizes of Li^+ and TBA^+ , it is natural that the former makes a larger change in the vibrational band assigned to the ionic association than the latter.

We shall demonstrate in this article that the increase in the relaxation frequency with the concentration predicted by our simulation and theoretical calculation is actually observed in TBATf solution, although there are some discrepancies between the calculations and experiment, while the increase in the relaxation frequency is not observed in LiTf solution. The difference between TBATf and LiTf is discussed in terms of the strength of the specific association. The disagreement between the theoretical calculation and experiment is also discussed.

2. EXPERIMENTAL METHODS

LiTf (Kishida Chemicals, 99%), TBATf (Sigma-Aldrich, 99%), and NaCl (Kishida Chemicals, 99.5%) are dried overnight under vacuum at 150 °C, 100 °C, and 150 °C, respectively, prior to use. THF (Kishida Chemicals, HPLC grade, 99.8%) and methanol (Kishida Chemicals, spectroscopic grade) are dried with Molecular Sieves 3A (Kishida Chemicals). THF- d_8 (Sigma-Aldrich, 99.5% d) is used as received for nuclear magnetic resonance (NMR) measurement.

The frequency-dependent conductivity is measured with the frequency-domain microwave reflectometry, which is described in detail elsewhere.²⁸ Briefly, a dielectric probe (HP85070B, Hewlett-Packard) attached to a vector network analyzer (HP8720D, Hewlett-Packard) is immersed into a sample liquid, and the complex reflectivity (S_{11}) of the microwave at the probe is measured as the function of the frequency. The frequency range of the measurement is from 50 MHz to 20 GHz. The reflectivity is converted into the dielectric spectrum of the sample, $\epsilon(\nu)$, by the three-point calibration method proposed by Wei and Srindhar.²⁹ Air, methanol,³⁰ and the aqueous solution of 1 M NaCl³¹ are employed as the reference. The temperature of the sample is controlled at 25.0 ± 0.1 °C by flowing thermostatted water within a jacket of the sample cell.

The direct-current (DC) conductivity is measured with a conductivity bridge and conductance cells. The density of the solution is measured with a vibrating tube densimeter (DMA602, Anton Paar).

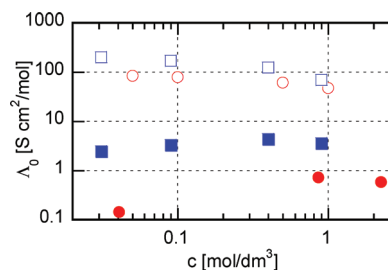


Figure 1. Molar conductivities experimentally determined (filled symbols) and estimated by the Nernst–Einstein relationship (open symbols) are plotted against concentration. The values of TBATf and LiTf are shown by blue and red symbols, respectively. The concentrations for the Nernst–Einstein values of LiTf are different from those for the conductivity because the former is taken from the literature.^{5,6}

The self-diffusion coefficients of the ions of LiTf solutions are reproduced from the paper by Saito and co-workers,^{5,6} and those of TBATf solutions are measured by us with the pulsed field gradient nuclear magnetic resonance (PFG-NMR) method. The spectrometer used is ECA600, manufactured by JEOL. The diffusion of Tf^- is monitored by the resonance of F-atoms and that of TBA^+ is by that of H-atoms of the terminal methyl group. During the measurement of the methyl group of TBA^+ , the radio wave resonant to the adjacent methylene group is irradiated in order to eliminate the effects of the coupling with methyl and methylene protons. The diffusion time, which is defined as the interval between the two field-gradient pulses, is adjusted between 13–21 ms according to the diffusion coefficient in order to optimize the quality of the decay profile of the echo intensity.

3. RESULTS AND DISCUSSION

Figure 1 shows the molar conductivities, denoted as Λ_0 , of TBATf and LiTf in THF at the concentration where frequency-dependent conductivity is measured. The molar conductivity increases with concentration on the lower concentration side, while it decreases on the higher concentration side. Since the molar conductivity must be a decreasing function of the concentration in the infinite dilution limit, there must be a minimum of molar conductivity below 1 mol/dm³, although it is not observed in this study. Detailed concentration dependence of the molar conductivities of these solutions are found in the literature,^{5,6,8} where the presence of a minimum and a maximum is clearly observed. The values of the molar conductivities are consistent with them. The concentrations of the molar conductivity minima in the literature are close to the lowest concentrations studied in this work. Our experiment thus covers the concentration region where molar conductivity increases with concentration.

The increase in the molar conductivity with concentration is observed in both TBATf and LiTf solutions, irrespective of the sizes of the cations, which supports the idea that the increase in molar conductivity is a phenomenon that is universal to electrolyte solutions in solvents of low polarity.⁸ Comparing the molar conductivities of TBATf and LiTf, the former is larger than the latter in spite of TBA^+ being larger than Li^+ .

The molar conductivity decreases with concentration on the higher concentration side, which is a typical behavior of electrolyte solutions irrespective of the dielectric constant of the solvent. There can be various explanations for the decrease. For example, the effects of interionic interaction are stronger at higher concentration. Large ionic aggregates may be formed. The increase

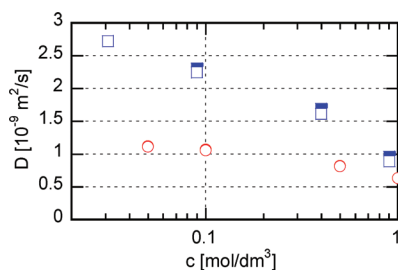


Figure 2. Self-diffusion coefficients of the cation (filled symbols) and the anion (open symbols) are plotted against concentration. The values of TBATf and LiTf are shown by blue and red symbols, respectively.

in the viscosity of the solution with the addition of salts may also contribute to the decrease. In our theoretical analysis, we found that the decrease can be attributed to the effects of short-range repulsive interactions between ions.²¹

The self-diffusion coefficients of ions are plotted in Figure 2 as the function of concentration. The diffusion coefficients of LiTf are taken from Saito and co-workers,^{5,6} and those of TBATf are measured in this work. The concentration of the former is different from that of the conductivity measurement because their experiment is performed at different concentrations. The self-diffusion coefficients are a decreasing function of the concentration in both solutions. The diffusion coefficients of the cation and anion are almost equal to each other in the case of LiTf, whereas a small difference is observed in the case of TBATf. The diffusion coefficients of TBATf are larger than those of LiTf, as is the case of the molar conductivity.

The Nernst–Einstein relationship describes the relationship between the molar conductivity and the self-diffusion coefficient of ions, which is given by

$$\Lambda_{\text{NE}} = \frac{F^2}{RT}(D_+ + D_-) \quad (1)$$

where F and R denote the Faraday and gas constants, respectively. The Nernst–Einstein relationship holds in the absence of the correlation between the motions of ions such as the infinite dilution limit.³² The Nernst–Einstein values of the molar conductivity are exhibited in Figure 1 together with the molar conductivity determined by conductometry. The former is more than 10 times larger than the latter, indicating the strong correlation between ions.

We have performed a Brownian dynamics simulation on a simple system in which ions are interacting through Coulombic and repulsive interactions.²⁰ The solvent is approximated as the dielectric continuum, and the hydrodynamic interactions between ions are neglected. We have succeeded in reproducing the molar conductivity minimum when the dielectric constant of the solvent is low, which supports the idea that the molar conductivity minimum is a phenomenon general to electrolyte solutions of low polarity. However, the self-diffusion coefficient also showed a small minimum, and the molar conductivity sometimes exceeded the Nernst–Einstein value, in contrast with the experiments as was shown in Figures 1 and 2. The simulation therefore failed to describe some characteristics of the experiments. We have suggested the potential of the mean force induced by the solvent, hydrodynamics interaction, and the polarizability of the ions as candidates to explain the discrepancy between the simulation and experiment, and we have to take these factors into account in order to explain the difference between Λ_0 and Λ_{NE} of the present

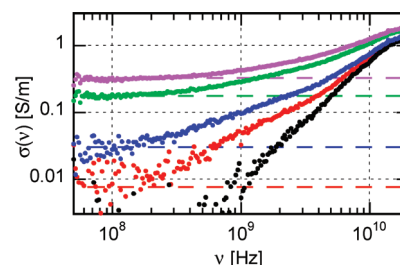


Figure 3. Frequency-dependent conductivities of THF solutions of TBATf are plotted against frequency. The concentrations are 0 mol/dm³ (black), 0.03 mol/dm³ (red), 0.09 mol/dm³ (blue), 0.4 mol/dm³ (green), and 0.9 mol/dm³ (purple). The broken lines indicate the values of DC conductivity at the corresponding concentrations.

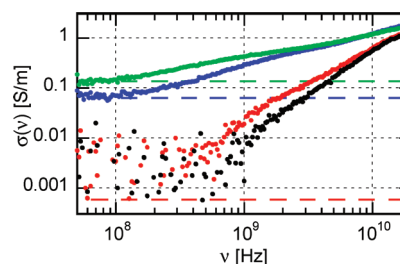


Figure 4. Frequency-dependent conductivities of THF solutions of LiTf are plotted against frequency. The concentrations are 0 mol/dm³ (black), 0.04 mol/dm³ (red), 0.9 mol/dm³ (blue), and 2.2 mol/dm³ (green). The broken lines indicate the values of DC conductivity at the corresponding concentrations.

systems. The reason for the small value of Λ_0 compared with that of Λ_{NE} is revisited later from the view of high-frequency molar conductivity.

It should be noted here that the molar conductivity far smaller than the Nernst–Einstein value is not always observed in electrolytes that show the molar conductivity minimum. The former is rather comparable to the latter in polyethylene-oxide based electrolytes where the molar conductivity minimum is often observed.^{17,33} Therefore, the mechanism for the molar conductivity minimum may not be required to explain the deviation of the molar conductivity from the Nernst–Einstein value at the same time.

Figures 3 and 4 show the alternating-current (AC) conductivities of TBATf and LiTf, respectively, at various concentrations as the function of frequency. The division of the complex dielectric spectrum into the dielectric relaxation and frequency-dependent conductivity is rather arbitrary, and we define the latter, denoted as $\sigma(\nu)$, in terms of the imaginary part of the dielectric spectrum, $\epsilon''(\nu)$, as

$$\sigma(\nu) \equiv 2\pi\nu\epsilon_0\epsilon''(\nu) \quad (2)$$

where ϵ_0 stands for the dielectric constant of the vacuum.

Equation 2 regards the dielectric response as the frequency-dependent conductivity, and it is usually employed in studies of supercooled ionic melts and ionic glasses.²² However, a different description has been employed in studies of electrolyte solutions as

$$\epsilon(\nu) = \Delta\epsilon(\nu) + \frac{\sigma_0}{2\pi i\nu\epsilon_0} \quad (3)$$

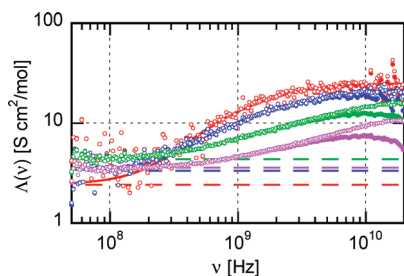


Figure 5. Frequency-dependent molar conductivities of THF solutions of TBATf are plotted against frequency. The concentrations are 0.03 mol/dm³ (red), 0.09 mol/dm³ (blue), 0.4 mol/dm³ (green), and 0.9 mol/dm³ (purple). Filled and open symbols indicate the values determined by eqs 4 and 5, respectively. These two symbols overlap with each other at $\nu < 5$ GHz. The broken lines indicate the values of DC conductivity at the corresponding concentrations. The spectra calculated with a model function, eq 6, are plotted with solid curves, which are almost overlapping the open circles.

where σ_0 means the DC conductivity.³⁴ In eq 3, the frequency-dependence of the dielectric response is wholly ascribed to $\Delta\epsilon(\nu)$, and it has been analyzed in the same way as the dielectric spectra of nonionic systems. In particular, eq 3 tempts us to assign the frequency dependence of $\Delta\epsilon(\nu)$ to the reorientational relaxations of molecules and ionic aggregates that possess dipole moments because $\epsilon(\nu)$ of nonionic systems are assigned to the reorientation of dipole moments. However, a difference between ionic and nonionic systems is that translational motion of ions can also contribute to $\Delta\epsilon(\nu)$ when the diffusive motion of ions is non-Markovian.^{22,35} Indeed, it was recently demonstrated that the translational motion of ions makes a significant contribution to the $\Delta\epsilon(\nu)$ of ionic liquids,^{36–39} although eq 3 has traditionally been applied in the field of ionic liquid.³⁴

The picture provided by eq 3 is not useful in the presence of the translational contribution, and we consider that eq 2 is a better description in such a case because the non-Markovian diffusion is equivalent to the frequency-dependent diffusivity. Our Brownian dynamics simulation showed that the non-Markovian dynamics is also present in cases of electrolyte solutions in weakly polar solvents,²⁰ and a purpose of this work is to examine the characteristics of the non-Markovian dynamics in real systems. It is the reason why we employ eq 2 in this work. However, it should of course be kept in mind that the reorientational relaxations of polar solvents and ionic aggregates, if any, also contribute to the frequency-dependent conductivity, $\sigma(\nu)$.

The conductivities of both salts are increasing functions of frequency at all the concentrations, as demonstrated in the figures. The conductivities converge to the corresponding DC values indicated by broken lines below 50 MHz within the experimental error in the presence of the electrolyte. Therefore, we can judge that the slow dynamics whose characteristic frequency is lower than 50 MHz is not coupled to the ionic conduction mechanism. Although the convergence to the DC value is not confirmed from Figure 4 in the case of LiTf at 0.04 mol/dm³, it is due to the experimental error of our measurement. From the scatter of the data on the neat solvent and solutions at low concentrations, the error of $\sigma(\nu)$ is estimated to be about 0.01 S/m. The AC conductivity of neat THF originates in the reorientational relaxation of the solvent molecules, and it is asymptotically proportional to ν^2 in the low-frequency limit. Since the AC conductivity of the neat solvent is comparable with those of the electrolyte solutions,

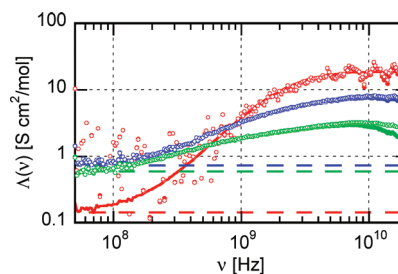


Figure 6. Frequency-dependent conductivities of THF solutions of LiTf are plotted against frequency. The concentrations are 0.04 mol/dm³ (red), 0.9 mol/dm³ (blue), and 2.2 mol/dm³ (green). Filled and open symbols indicate the values determined by eqs 3 and 4, respectively. These two symbols overlap with each other at $\nu < 8$ GHz. The broken lines indicate the values of DC conductivity at the corresponding concentrations. The spectra calculated with a model function, eq 6, are plotted with solid curves, which are almost overlapping the open circles.

we have to subtract the contribution of the solvent to the conductivity in some way in order to extract the information on the frequency-dependent mobility of ions.

We first try the simplest definition of the frequency-dependent molar conductivity, $\Lambda_1(\nu)$, given by

$$\Lambda_1(\nu) \equiv \frac{1}{c}[\sigma(\nu; c) - \sigma(\nu; c = 0)] \quad (4)$$

where c stands for the molar concentration of salts. The assumption of eq 4 is that the contribution of the solvent to the conductivity is not affected by the presence of ions. The results are shown as the filled symbols in Figures 5 and 6. The frequency-dependent conductivity, $\Lambda_1(\nu)$, increases with frequency below 10 GHz and decreases at higher frequencies. The molar AC conductivities converge to the corresponding DC values at 50 MHz as is indicated in Figures 3 and 4. Although the data points appear to scatter above the DC line at the lowest concentrations and $\nu < 100$ MHz, there actually exist many points below the lower limitation of the longitudinal axis of the graphs, and we judge that the convergence to the DC values is achieved at 50 MHz.

The AC ionic conductivity is an increasing function of frequency when the ionic conduction is coupled to slow relaxation modes. The dispersion of the conductivity occurs at the frequency corresponding to the relaxation time of the slow mode, and it converges to the bare value, that is, the mobility without interionic interaction, determined by the Markovian friction from the solvent.²² In molecular dynamics simulations, a resonance peak is often observed in the THz region, which is ascribed to the vibration of ions in a cage, and the conductivity decreases at higher frequencies.^{40,41} Since the peak frequency of $\Lambda_1(\nu)$ is about 10 GHz, it is too low to be assigned to the resonance peak, and there is no other physical mechanism for the peak of $\Lambda(\nu)$ to our best knowledge.

We consider that the decrease in the molar conductivity at $\nu > 10$ GHz is because eq 4 overestimates the contribution of the solvent to the conductivity. The AC conductivity due to the reorientational relaxation of the solvent can decrease by increasing the concentration of salts due to two reasons. The first one is because the number density of the solvent decreases with the concentration of salts due to the exclusion volumes of ions, and the second one is because the reorientational motion of the solvent is

Table 1. Parameters in eq 6 That Reproduce the Spectra in Figures 5 and 6

solute	concentration (mol/dm ³)	Λ_0 (S cm ² /mol)	τ_1 (ps)	Λ_i (S cm ² /mol)	τ_2 (ps)	Λ_∞ (S cm ² /mol)
TBATf	0.031	2.4	250	15	70	25
	0.090	3.3	220	13	40	22
	0.40	4.3	180	9	25	17
	0.90	3.6	130	6	19	12
LiTf	0.041 ^a	0.14	75	20		20
	0.86	0.72	230	4	40	9.5
	2.2	0.59	350	2	38	4.2

^aThe single Debye function was used.

restricted due to the strong Coulombic interaction between an ion and a solvent.^{34,42}

The effect of the excluded volume can easily be included with a simple modification of eq 4 as

$$\Lambda_2(\nu) \equiv \frac{1}{c} \left[\sigma(\nu; c) - \frac{\rho_s(c)}{\rho_s(c=0)} \sigma(\nu; c=0) \right] \quad (5)$$

where $\rho_s(c)$ stands for the number density of the solvent when the concentration of the salt is equal to c . The results are exhibited by the open symbols in Figures 5 and 6. The molar AC conductivity of TBATf appears to have a plateau on the high-frequency side, which tempts to assign the plateau values to the bare conductivity of the solution. However, the decrease in $\Lambda_2(\nu)$ is observed on the high-frequency side in the case of LiTf. We consider that it is because the restriction of the reorientational motion of solvent by LiTf is strong, as is expected from the small ionic size of Li⁺. The difference between $\Lambda_1(\nu)$ and $\Lambda_2(\nu)$ is negligible at $\nu < 5$ GHz in the cases of both solutions.

In order to parametrize $\Lambda_2(\nu)$, we try to reproduce them with a model function given by

$$\Lambda_2(\nu) = \Lambda_\infty - \frac{\Lambda_\infty - \Lambda_i}{1 + (2\pi\nu\tau_2)^2} - \frac{\Lambda_i - \Lambda_0}{1 + (2\pi\nu\tau_1)^2} - \frac{n}{\rho_s(c=0)} \sigma(\nu; c=0) \quad (6)$$

where Λ_0 is the molar DC conductivity determined with DC conductometry, and Λ_∞ , Λ_i , τ_1 , and τ_2 are parameters that characterize the molar conductivity spectra. The relaxation amplitudes of the faster and slower processes are given by $\Lambda_\infty - \Lambda_i$ and $\Lambda_i - \Lambda_0$, respectively, and Λ_∞ stands for the molar conductivity in the high-frequency limit. The last term is introduced in order to describe the restriction of the reorientational motion of the solvent by salts, and the parameter n denotes the strength of the restriction. The values of n are fixed to 0 and 1.5 for TBATf and LiTf, respectively, which are determined to reproduce the high-frequency behavior of $\Lambda_2(\nu)$. Although the molar conductivity spectra are described as the sum of two Debye functions, it should be noted that we do not intend to claim that there are two distinct processes or chemical species.

Table 1 shows the parameters used for the reproduction of the spectra in Figures 5 and 6. The calculated spectra are compared with experimental ones in Figures 5 and 6. The former describes the latter fairly well. In the case of LiTf at 0.04 mol/dm³, the single Debye function, that is, $\Lambda_i = \Lambda_\infty$, is sufficient to reproduce the spectrum.

Now we turn our attention to the way the molar conductivity dispersion varies with increasing concentrations of salts. Figure 5 shows that the relaxation frequency of the molar conductivity shifts to the high frequency side with concentration. The shift of the relaxation frequency is also confirmed by the decrease in the relaxation times shown in Table 1. The AC molar conductivity is a monotonically decreasing function of the concentration at $\nu > 500$ MHz. Therefore, we can ascribe the increase in molar DC conductivity with concentration to the relaxation process exhibited in Figure 5. Since the decrease in the relaxation time with concentration is just what we have observed in our Brownian dynamics simulation, we consider that the mechanism of molar conductivity minimum in our simulation is also working in the THF solution of TBATf.

The situation appears different in the case of LiTf, as is shown in Figure 6 and Table 1. The convergence to the DC conductivity is slower at higher concentration in Figure 6, which corresponds to the presence of the slower component in Table 1. The dispersion of the conductivity is often observed in electrolyte solutions, and it has been assigned to the reorientational relaxation of ion pairs.^{19,34,42–44} A small relaxation is sometimes found on the low-frequency side of the relaxation ascribed to the ion pair when the polarity of the solvent is low and the concentration of the salt is high, and it has been assigned to the reorientational relaxation of triple ions.^{19,42,43} The triple ion may contribute to the dielectric relaxation if its charge distribution is asymmetric, and the relaxation time of triple ion is expected to be longer than that of the ion pair because the size of the former is larger than that of the latter. The slower convergence to the DC conductivity of the LiTf solution at higher concentration may be explained in terms of the presence of the reorientational relaxation of triple ions at several hundreds MHz.

The interpretation of the conductivity dispersion of TBATf solution in terms of the ionic association is difficult, as has already been discussed in ref 20. Under the assignment of the relaxation to the reorientational relaxation of an ion pair, the increase in the relaxation frequency with concentration means the decrease in the reorientational relaxation time of an ion pair, which is difficult to understand because the interaction of an ion pair with other ions becomes stronger with increasing concentration. The introduction of additional relaxation due to triple ions cannot resolve the problem because its reorientational relaxation is slower than that of the ion pair.

The increase in the relaxation frequency of conductivity was already reported for TBA salt solutions. Cachet and Lestrade measured the dielectric relaxation spectra of tributylammonium and TBA salts in benzene in the microwave frequency region.²⁴ The relaxation frequency of the former decreases, while that of the latter increases with concentration. They assigned the relaxation of the former to the reorientational relaxation of ion pairs, whereas that of the latter is ascribed to the collective translational motion of ions. They elucidated the difference between them to the specific hydrogen-bonding interaction in the former system. Our present discussion on the triflate salt solutions is in harmony with theirs. However, we should note here that their assignment was based on the relaxation amplitude, not on the relaxation time, and they did not give any explanation for the decrease in the relaxation frequency with concentration.

Vibrational spectroscopy has shown that the vibrational band of Tf[−] in LiTf solution exhibits the structure assigned to the Li-Tf ion pair when the dielectric constant of the solvent is low.¹³ In addition, an additional band is sometimes observed, and it is ascribed

to the Li_2Tf^+ triple ion.¹³ However, TBATf does not show a band assigned to ion pairs.⁷ The difference in the Raman spectra of LiTf and TBATf is natural because the smaller size of Li^+ promotes ionic association, and the effects on vibrational modes of Tf^- can also be stronger.

Given the difference in the vibrational spectra of LiTf and TBATf, it seems a reasonable idea to interpret their conductivity dispersion spectra in different ways. The dispersion of LiTf solution is assigned to the reorientation of ion pairs and triple ions, whereas that of TBATf to the collective translational dynamics of ions was as suggested by our theoretical calculation.²¹ Such assignments mean that the mechanisms of the molar conductivity are different for these salts. However, we do not consider that only one mechanism is working in each solution. Rather, both the collective dynamics and ionic association may be present in both solutions, and the difference is the relative contribution of each mechanism.

We consider that a difference between the TBATf and LiTf solutions lies in the strength of the specific association between a cation and an anion. The behavior of the former is closer to our Brownian dynamics simulation because the specific interaction is not included in the simulation. The ions are interacting with each other merely through the electrostatic and repulsive interactions, and the specific association expected for the LiTf solution is not taken into account there. Although we have also performed simulations with solvent-induced potential of mean force between ions that behave as a barrier to prevent the dissociation of the contact ion pair, the height of the barrier is not high enough to reproduce the experimentally observed behaviors. The increase in molar conductivity of TBATf and LiTf solutions with concentration should in principle be understood in a unified way, and we consider it indispensable to study the collective dynamics of electrolyte solutions with strong specific association.

In addition to the conductivity dispersion observed experimentally between 50 MHz and 20 GHz, we should pay attention to the difference between the molar conductivity at 20 GHz and that estimated from the Nernst–Einstein relationship. The molar AC conductivities shown in Figures 5 and 6 appear to show plateaus in the 10 GHz region, and the values of Λ_∞ in Table 1 are close to the corresponding values at 20 GHz. The high-frequency mobility is usually interpreted as the bare mobility. Since the zero-frequency self-diffusivity should also be affected by slow dynamics, the self-diffusion coefficient determined by NMR must be smaller than the bare mobility of ions. Therefore, the smaller values of molar AC conductivities at 20 GHz than the Nernst–Einstein ones indicate that the former are actually not the bare mobilities and that there must be relaxation processes at higher frequencies. The largest discrepancy between our Brownian dynamics simulation and experiments is that the DC conductivity is similar to the Nernst–Einstein value in our simulation, and the reason for the large difference between DC mobilities, $\Lambda_0 \ll \Lambda_{\text{NE}}$, lies in the dynamics faster than 20 GHz.²⁰

The discrepancy of the DC conductivity from the Nernst–Einstein relationship is usually discussed in terms of the ion pair formation.³² Since an ion pair contributes to the self-diffusion coefficient while not to the conductivity, the reduction of the conductivity by the ion pair formation is larger than that of the self-diffusion coefficient. Thus, we first examine how the conductivity dispersion behaves if the ion pair formation is mainly responsible to the reduction of the conductivity.

In the simplest picture of the ion pair formation, two ions are bound to each other through the interionic force that is parallel to

the vector connecting two ions, and the random force on ions from the solvents is not affected by the association. The interionic force may be the direct one or the mean force through the solvent. The motion of each ion pair is uncorrelated.

One of the assignments of the conductivity dispersion in the microwave region is the reorientational relaxation of the ion pair. The conductivity of an ion pair is zero in the zero frequency limit. It increases with frequency around the reorientational relaxation frequency and converges to the value determined by the mobility of each ion in the direction perpendicular to the interionic vector. The high-frequency limiting value is thus two to the third of the bare mobility under the assumption described in the previous paragraph. The molar AC conductivity at 20 GHz obviously indicates that the assignments above do not hold for systems studied here.

Considering the size and dipole moment of the LiTf ion pair, its reorientational relaxation time should be comparable to or larger than that of THF. The molar AC conductivity of the LiTf solution at 20 GHz is thus interpreted as the molar conductivity at the frequency higher than the reorientational relaxation time. Therefore, the ion pair formation should reduce the mobility of each ion in the direction perpendicular to the interionic vector. The simplest idea is that the interionic force may not be parallel to the interionic vector because the Tf^- ion is not spherical. The presence of another ion may alter the interaction between the ion and solvents through the modification of the solvent structure. The hydrodynamic interaction is also a candidate, because the force on an ion exerted through the hydrodynamic interaction is not parallel to the interionic vector.

Our theoretical calculation showed that there are two relaxations in the conductivity dispersion of the model system without specific association.²¹ The faster relaxation reflects the collision between a cation and an anion, and the slower one does the collective motion of ions. The amplitude of the former is much smaller than that of the latter at the concentration near the molar conductivity minimum. Therefore, the faster relaxation revealed by the theoretical calculation does not explain the discrepancy between the molar AC conductivity at 20 GHz and the Nernst–Einstein value.

We consider that the hydrodynamic interaction is the most possible reason for the small molar AC conductivity of both salts at 20 GHz. Since the hydrodynamic interaction works between a pair of ions without specific association, it can be a reason for the reduction of the 20 GHz conductivities of both TBATf and LiTf. Theoretically, the hydrodynamic interaction directly reduces the molar conductivity, whereas it affects the self-diffusion coefficient merely indirectly, and its effect on conductivity is as large as that of the relaxation of the ionic atmosphere.^{45,46} We can estimate the time scale in which the hydrodynamic interaction works based on the continuum picture. The kinematic viscosity of THF is $0.5 \text{ mm}^2/\text{s}$ at 25°C ,²⁶ and momentum can diffuse up to a 2 nm distance during 8 ps, which corresponds to 20 GHz. The hydrodynamic interaction works through the diffusion of momentum within the solvent. Since the Debye screening length is smaller than 2 nm at all the concentrations studied here, the decrease in the molar conductivity due to the hydrodynamic interaction occurs at $\nu > 20 \text{ GHz}$. The discussion above is a rough estimate, and we should consider the viscous momentum transfer at the molecular scale for quantitative discussion.

Although it is in principle desirable to probe the dynamics at $\nu > 20 \text{ GHz}$ experimentally because it must contain important information on the relationship between ionic conductivity and self-diffusivity, it would be difficult due to the large contribution

of the solvent to the high-frequency dielectric response. Theoretical and computational studies will thus be required in order to resolve the high-frequency dynamics.

4. SUMMARY

We have measured the frequency-dependent AC conductivities of TBATf and LiTf solutions in THF at 50 MHz–20 GHz. The dispersion of the molar AC conductivity is found in both solutions, and the AC conductivity converges to the DC one at 50 MHz. The molar AC conductivity at 20 GHz is a decreasing function of concentration, whereas the molar DC conductivity increases. Therefore, the relaxation observed at 50 MHz–20 GHz is the reason for the increase in the molar DC conductivity with concentration.

The relaxation becomes faster with increasing concentration in the case of TBATf as was observed in our Brownian dynamics simulation.²⁰ The theoretical analysis of the simulation has shown that the collective dynamics of ions is the reason for the increase in the relaxation frequency,²¹ which elucidates the increase in the molar DC conductivity as is observed in experiments. We believe that the increase in the relaxation frequency in the case of TBATf is the largest finding in this work because it plays a central role in our mechanism of the increase in molar DC conductivity. Although the increase in the relaxation frequency itself was already reported experimentally by Cachet and Lestrade,²⁴ there has been no explanation for it to our best knowledge, except for that we have proposed based on our theoretical calculations.^{20,21} We consider that the increase in the relaxation frequency of TBATf in THF strongly supports our mechanism, although the improvement of the model is necessary on some points.

However, the increase in the relaxation frequency with concentration is not always observed when the molar DC conductivity increases. In the case of the LiTf solution, the low-frequency side of the spectrum grows, and the convergence to the DC conductivity becomes slower with increasing concentration. It is in harmony with a conventional assignment of the dielectric relaxation to the reorientational relaxations of the ion pair and triple ions, suggesting that the triple ion plays a certain role in the increase in the molar DC conductivity. The difference between TBATf and LiTf is in harmony with vibrational spectroscopic studies, in which LiTf shows the band ascribed to the ion pair and the triple ion, whereas no such bands are observed in TBATf solutions. However, we consider that the theoretical analysis of collective ionic dynamics in the presence of the specific interaction is required in order to understand the conduction mechanism of TBATf and LiTf solutions quantitatively.

The conductivities of both salts at 20 GHz are about an order of magnitude smaller than the corresponding values of the Nernst–Einstein relationship estimated from the self-diffusion coefficients of ions. The presence of the relaxation processes at higher frequency is thus expected, and we consider that the hydrodynamic interaction between ions is the most probable mechanism.

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REFERENCES

- (1) Bockris, J.; Reddy, A. *Modern Electrochemistry*; Plenum Press: New York, 1970; Vol. 1, Chapter 4.
- (2) Fuoss, R. M.; Kraus, C. A. *J. Am. Chem. Soc.* **1933**, *55*, 21.
- (3) Cavell, E. A. S.; Knight, P. C. *Z. Phys. Chem.* **1968**, *57*, 331.
- (4) Delsignore, M.; Farber, H.; Petrucci, S. *J. Phys. Chem.* **1985**, *89*, 4968.
- (5) Saito, Y.; Yamamoto, H.; Nakamura, O.; Kageyama, H.; Ishikawa, H.; Miyoshi, T.; Matsuoka, M. *J. Power Sources* **1999**, *81–82*, 772.
- (6) Saito, Y.; Yamamoto, H.; Kageyama, H.; Nakamura, O.; Miyoshi, T.; Matsuoka, M. *J. Mater. Sci.* **2000**, *35*, 809.
- (7) Petrowsky, M.; Frech, R.; Suarez, S. N.; Jayakody, J. R. P.; Greenbaum, S. *J. Phys. Chem. B* **2006**, *110*, 23012.
- (8) Petrowsky, M.; Frech, R. *J. Phys. Chem. B* **2008**, *112*, 8285.
- (9) Petrucci, S.; Masiker, M. C.; Eyring, E. M. *J. Solution Chem.* **2008**, *37*, 1031.
- (10) Palval, I. N.; Lebed, A. V.; Mchedlov-Petrosyan, N. O. *J. Mol. Liq.* **2011**, *158*, 33.
- (11) Cameron, G. G.; Ingram, M. D.; Sorrie, G. A. *J. Electroanal. Chem.* **1986**, *198*, 205.
- (12) Gray, F. M. *Solid State Ionics* **1990**, *40/41*, 637.
- (13) Albinsson, I.; Mellander, B.-E.; Stevens, J. R. *J. Chem. Phys.* **1992**, *96*, 681.
- (14) Ferry, A.; Jacobsson, P.; Torell, L. M. *Electrochim. Acta* **1995**, *13/14*, 2369.
- (15) Borodin, O.; Douglas, R.; Smith, G.; Eyring, E. M.; Petrucci, S. *J. Phys. Chem. B* **2002**, *106*, 2140.
- (16) Petrucci, S.; Eyring, E. M. *Phys. Chem. Chem. Phys.* **2002**, *4*, 6043.
- (17) Walls, H. J.; Fedkiw, P. S.; Zawodzinski, T. A., Jr.; Khan, S. A. *J. Electrochem. Soc.* **2003**, *150*, E165.
- (18) Barthel, J.; Krienke, H.; Neueder, R.; Holovko, M. F. *Fluid Phase Equilib.* **2002**, *194*, 107.
- (19) Marcus, Y.; Hefter, G. *Chem. Rev.* **2006**, *106*, 4585.
- (20) Yamaguchi, T.; Akatsuka, T.; Koda, S. *J. Chem. Phys.* **2011**, *134*, 244506.
- (21) Yamaguchi, T.; Matsuoka, T.; Koda, S. Unpublished data.
- (22) Funke, K.; Banhatti, R. D.; Brückner, S.; Cramer, C.; Krieger, C.; Mandanici, A.; Martiny, C.; Ross, I. *Phys. Chem. Chem. Phys.* **2002**, *4*, 3155.
- (23) Davies, M.; Williams, G. *Trans. Faraday Soc.* **1960**, *56*, 1619.
- (24) Cachet, H.; Lestrade, J. C. *Bull. Soc. Chim. Belg.* **1976**, *85*, 481.
- (25) Weingärtner, H.; Nadolny, H. G.; Käshammer, S. *J. Phys. Chem. B* **1999**, *103*, 4738.
- (26) Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents*, 4th ed.; John Wiley & Sons: New York, 1986.
- (27) Kato, Y.; Ishihara, T.; Uchimoto, Y.; Wakihara, M. *J. Phys. Chem. B* **2004**, *108*, 4794.
- (28) Yamaguchi, T.; Hayakawa, M.; Matsuoka, T.; Koda, S. *J. Phys. Chem. B* **2009**, *113*, 11988.
- (29) Wei, Y.-Z.; Sridhar, S. *IEEE Trans. Microwave Theory Tech.* **1991**, *39*, 526.
- (30) Buchner, R. Private communication.
- (31) Buchner, R.; Hefter, G. T.; May, P. M. *J. Phys. Chem. A* **1999**, *103*, 1.
- (32) Harris, K. R. *J. Phys. Chem. B* **2010**, *114*, 9572.
- (33) Hayamizu, K.; Akiba, E.; Bando, T.; Aihara, Y. *J. Chem. Phys.* **2002**, *117*, 5929.
- (34) Buchner, R.; Hefter, G. *Phys. Chem. Chem. Phys.* **2009**, *11*, 8984.

- (35) Schröder, C.; Haberler, M.; Steinhauser, O. *J. Chem. Phys.* **2008**, *128*, 134501.
- (36) Yamaguchi, T.; Koda, S. *J. Chem. Phys.* **2010**, *132*, 114502.
- (37) Schröder, C.; Sonnleitner, T.; Buchner, R.; Steinhauser, O. *Phys. Chem. Chem. Phys.* **2011**, *13*, 12240.
- (38) Schröder, C. *J. Chem. Phys.* **2011**, *135*, 024502.
- (39) Yamaguchi, T.; Koda, S. *J. Mol. Liq.* 2011, DOI: 10.1016/j.molliq.2011.03.012.
- (40) Chowdhuri, S.; Chandra, A. *J. Chem. Phys.* **2001**, *115*, 3732.
- (41) Sala, J.; Guàrdia, E.; Martí, J. *J. Chem. Phys.* **2010**, *132*, 214505.
- (42) Wachter, W.; Fernandez, S.; Buchner, R.; Hefter, G. *J. Phys. Chem. B* **2007**, *111*, 9010.
- (43) Xu, M.; Petrucci, S.; Eyring, E. M. *J. Electroanal. Chem.* **1996**, *401*, 45.
- (44) Akiran, C.; Rohman, N.; Hefter, G.; Buchner, R. *ChemPhysChem* **2006**, *7*, 2319.
- (45) Jardat, M.; Bernard, O.; Turq, P.; Kneller, G. R. *J. Chem. Phys.* **1999**, *110*, 7993.
- (46) Jardat, M.; Durand-Vidal, S.; Turq, P.; Kneller, G. R. *J. Mol. Liq.* **2000**, *85*, 45.