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Solvation structure and dynamics of Li⁺ in Lewis-basic ionic liquid of 1-octyl-4-aza-1-azoniabicyclo[2.2.2]octane bis(trifluoromethanesulfonyl)amide



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1. Introduction

Ionic liquids (ILs) have been increasingly used as alternative solvents for lithium secondary batteries because of their low-volatility and lowflammability over conventional organic solvents [1]. The solvation structure and dynamics of Li⁺ in ILs on the microscopic scale is the key to design novel ILs which are more appropriate for battery electrolytes than conventional ones. There have been many experimental and simulation studies on the solvation structure and dynamics of Li⁺ in IL solutions with bis(trifluoromethanesulfonyl)amide (TFSA⁻) [2–23]. At low Li⁺ concentrations, a Li⁺ in TFSA⁻-IL solutions is solvated by a few TFSA⁻ as mono- and/or bidentate ligand. At high Li⁺ concentrations, on the other hand, several Li⁺ ions are bridged by TFSA⁻ to form Li⁺-TFSA⁻ polymer [4]. The bridging of Li⁺ by TFSA⁻ reduces the mobility of Li⁺ in the solutions. To enhance the mobility of Li⁺ in the IL solutions at high Li⁺ concentrations, Li⁺ should be inhibited from bridging with TFSA⁻. If Li⁺ will be solvated by the cation of IL, interactions between Li⁺ and TFSA⁻ become weaker. However, Lewisacidic cations such as imidazolium and pyrrolidinium cannot solvate Li⁺.

ILs involving 1-alkyl-4-aza-1-azoniabicyclo[2.2.2]octane (C_n dabco⁺) may solvate Li⁺ because the IL cation has Lewis base property due to a tertiary nitrogen atom with a lone pair at the position 4 (see Fig. 1 for the

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ABSTRACT

¹H, ⁷Li, ¹³C, ¹⁵N, and ¹⁹F NMR spectra of 1-octyl-4-aza-1-azoniabicyclo[2.2.2]octane bis(trifluoromethanesulfonyl) amide ([C₈dabco][TFSA]) solutions with and without LiTFSA (lithium mole fractions of $x_{Li} = 0$ and 0.1) were measured at 313.2 K. The chemical shift measured for each nucleus was corrected for volume magnetic susceptibility of the solution. For comparison, those NMR spectra of 1-methyl-3-octylimidazolium bis(trifluoromethanesulfonyl) amide ([C₈mim][TFSA]) solutions were recorded under the same condition. The peak shifts for the nuclei induced by the dissolution of Li⁺ showed that Li⁺ interacts with not only TFSA⁻ but also C₈dabco⁺ in [C₈dabco][TFSA] solution. Self-diffusion coefficients of the cation, anion, and Li⁺ in the ionic liquid solutions were determined by a pulsed field gradient NMR technique. Correlation times for jump motion of Li⁺ were estimated from ⁷Li longitudinal relaxation times with two different magnetic fields. The diffusion and jump motions of Li⁺ in [C₈dabco][TFSA] and [C₈mim][TFSA] solutions are discussed in terms of interionic interactions.

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position-numbers of the atoms) [24,25]. The solvation structure and dynamics of Li⁺ in Lewis-basic IL solutions may differ from those in Lewisacidic IL solutions. As far as we know, however, any information on the solvation structure and dynamics of Li⁺ in ILs consisting of C_ndabco⁺ has not been available. In this study, to clarify the solvation structure of Li⁺ in IL with C_ndabco⁺, we have made NMR measurements for ¹H, ⁷Li, ¹³C, ¹⁵N, and ¹⁹F nuclei in 1-octyl-4-aza-1-azoniabicyclo[2.2.2]octane bis(trifluoromethanesulfonyl)amide ([C₈dabco][TFSA]) solutions with LiTFSA at the Li⁺ mole fractions of $x_{\text{Li}} = 0$ and 0.1. The results of C₈dabco⁺-IL solutions were compared with those of 1-methyl-3octylimidazolium bis(trifluoromethanesulfonyl)amide ([C₈mim][TFSA]) solutions. Moreover, ionic self-diffusion coefficients and ⁷Li longitudinal relaxation times were determined to evaluate the dynamics of Li⁺ in both ILs. Fig. 1 shows the molecular structures of C₈dabco⁺ and C₈mim⁺ with the position-numbers according to the IUPAC numeration.

2. Experimental

Lewis-basic IL of $[C_8dabco]$ [TFSA] was synthesized according to the literature [25]. Each of 1,4-diazabicyclo[2.2.2]octane (>99%, Sigma-Aldrich) and 1-bromooctane (>98.0%, Tokyo Kasei) was dissolved in ethyl acetate (>99.5%, Wako). The 1-bromooctane solution was dropped into the solution of fivefold molar amount of 1,4-diazabicyclo[2.2.2]octane with cooling by ice. The mixed solution was stirred at room temperature for 24 h or more. The crude salt of



Fig. 1. Molecular structures of C_8 dabco⁺ and C_8 mim⁺ with the position-numbers in the parentheses according to the IUPAC numeration.

[C₈dabco]Br was precipitated in the solution. Ethyl acetate phase was removed by filtration, and ethyl acetate adsorbed on the salt was removed by heating at ~343 K for 6 h under vacuum. The salt was recrystallized twice from isopropyl alcohol (>99.7%, Wako). The refined salt of [C₈dabco]Br was filtrated from the solvent, and then the solvent was evaporated at ~343 K for 6 h under reduced pressure. On the contrary, [C₈mim]Br was obtained from the reaction of 1-methylimidazole (>99.0%, Tokyo Kasei) with 1-bromooctane in acetonitrile (>99.8%, Wako) by the conventional method [26]. The salt of [C₈mim]Br was recrystallized from toluene (>99.8%, Wako). The refined salt of [C₈mim]Br was heated at ~343 K for 6 h under reduced pressure to remove the excess solvent. Aqueous solutions of KTFSA (>99.8%, Kanto Kagaku) and HTFSA (>99.0%, Kanto Kagaku) were added to aqueous solutions of [C₈dabco]Br and [C₈mim]Br, respectively, to replace Br⁻ with TFSA⁻ . Note that in the synthesis of [C₈dabco][TFSA] highly Lewis-acidic ions, such as H⁺ and Li⁺, cannot be used as the counter cation of TFSA⁻ because such ions strongly interact with Lewis-basic tertiary amine of C₈dabco⁺. After stirring the biphasic mixture of each IL system for 24 h, the upper aqueous phase was decanted, and then the lower nonaqueous phase was washed more than five times with pure water (Millipore, Elix UV 3 water purification systems). Water in the IL phase was removed under vacuum at ~323 K for 8 h or more. Finally, each colorless viscous liquid of [C₈dabco][TFSA] and [C₈mim][TFSA] thus obtained was identified by ¹H and ¹³C NMR spectroscopic measurements and elemental analyses for the H, C, and N atoms; Anal. Calc. (%) for C₁₆H₂₉N₃O₄F₆S₂ (C₈dabcoTFSA): C, 38.01, H, 5.78, N, 8.31, Found: C, 37.96, H, 5.65, N, 8.58 and Anal. Calc. (%) for C₁₄H₂₃N₃O₄F₆S₂ (C₈mimTFSA): C, 35.36, H, 4.88, N, 8.84, Found: C, 35.44, H, 4.82, N, 9.03. These results showed no major organic impurity in both ILs. Moreover, residual Br⁻ in the ILs could not be detected by a fluorescence Xray analysis (Shimadzu, Rayny EDX-800HS). The water contents of [C₈dabco][TFSA] and [C₈mim][TFSA] were determined by a Karl-Fisher titration to be 73 and 70 ppm, respectively. LiTFSA (>99.95%, Sigma-Aldrich) was dissolved into each IL at $x_{Li} = 0.1$ under nitrogen atmosphere.

Density (ρ), viscosity (η), and electrical conductivity (κ) of pure ILs and LiTFSA-IL solutions were determined at 313.2 K using the same equipments as those in the previous report [27].

NMR spectra of ¹H, ⁷Li, ¹³C, ¹⁵N, and ¹⁹F nuclei were recorded on the Agilent 400 MHz NMR system. A double tube was constructed from a 3.0 mm ϕ inner tube (Shigemi, PN-001) including the reference solution

and a 5.0 mm ϕ outer tube (Shigemi, PS-001-7) containing sample solution for the chemical shift measurements. A 0.75 wt.% 3-(trimethylsilyl)propionic-2,2,3,3- d_4 acid (TSP) in D₂O solution (Sigma-Aldrich), 3.00 mol dm⁻³ lithium chloride (>99.99%, Sigma-Aldrich) in D₂O (99.96 at.%D, Sigma-Aldrich), nitromethane- d_3 (99 at.%D, Sigma-Aldrich), and hexafluorobenzene (>99.5%, Sigma-Aldrich) were used as external references for ¹H and ¹³C, ⁷Li, ¹⁵N, and ¹⁹F nuclei, respectively.

Self-diffusion coefficient measurements were conducted on pure ILs and LiTFSA-IL solutions using the JEOL ECA-600 spectrometer. To suppress convection flow as much as possible, an NMR microtube (Shigemi, DMS-005]) was used in the diffusion experiments. The sample solution in the NMR tube was less than 5 mm in height. Self-diffusion coefficients of D_{cation} , D_{anion} , and D_{Li} were determined from ¹H NMR peak of the terminal methyl group of the cations, ¹⁹F and ⁷Li peaks of TFSA⁻ and Li⁺, respectively. A pulsed field gradient spin-echo sequence was used in all the self-diffusion coefficient measurements. The diffusion time was fixed at 100 ms. The gradient magnitude (g) or the gradient pulse width (δ) was varied during the measurements. The gradient magnitudes were calibrated using the self-diffusion coefficient of water at 313.2 K [28]. The self-diffusion coefficients determined from both methods with varying g and δ were in good agreement with each other within the deviation of \pm 3%. The self-diffusion coefficients determined by both methods were averaged to obtain the final values.

⁷Li longitudinal relaxation times ($T_{1,Li}$) were measured using the above two NMR spectrometers. The sample solutions were sealed into NMR microtubes (Shigemi, SP-001). A standard inversion recovery sequence was used in the $T_{1,Li}$ measurements.

3. Results and discussion

3.1. Density (ρ), viscosity (η), and electrical conductivity (κ)

The ρ , η , and κ values at 313.2 K are summarized in Table 1. The ρ value of pure [C_8 mim][TFSA] agrees with the literature data within \pm 1% [29–31]. The other physicochemical properties of the C_8 dabco⁺- and C_8 mim⁺-IL systems at the temperature investigated are unfortunately unavailable in the literature. For both IL systems, the ρ and η values increase by the dissolution of Li⁺ into the ILs, while the κ values decrease. These features are comparable with the previous results of pyrrolidinium- and ammonium-ILs [2,8,10,14]. The molar conductivities (Λ) of the IL solutions at $x_{Li} = 0$ and 0.1 were estimated from the values of ρ and κ by

$$\Lambda = \frac{\kappa \times M_{\text{mix}}}{\rho},\tag{1}$$

Table 1

Densities (ρ), viscosities (η), electrical conductivities (κ), molar conductivities (Λ), Walden products (η Λ), self-diffusion coefficients (D_{cation} , D_{anion} , D_{Li}), Nernst–Einstein deviation parameters (Δ), and hydrodynamic radii of cation (r_{cation}), anion (r_{anion}), and Li⁺ (r_{Li}) in C₈dabco⁺- and C₈mim⁺-IL solutions with LiTFSA at $x_{Li} = 0$ and 0.1 and 313.2 K.

IL	[C ₈ dabco][TFSA]		[C ₈ mim][TFSA]	
X _{Li}	0	0.100	0	0.100
$ ho/{ m g~cm^{-3}}$	1.32	1.34	1.31	1.33
η/mPa s	276	543	47.7	60.3
$\kappa/S m^{-1}$	0.0375	0.0207	0.246	0.199
$\Lambda/10^{-5} \mathrm{S}\mathrm{m}^2\mathrm{mol}^{-1}$	1.44	0.748	8.95	6.85
$\eta\Lambda/10^{-6}$ Pa s S m ² mol ⁻¹	3.98	4.06	4.27	4.13
$D_{\text{cation}}/10^{-11} \text{ m}^2 \text{ s}^{-1}$	0.34	0.19	2.4	1.9
$D_{\rm anion}/10^{-11} {\rm m}^2 {\rm s}^{-1}$	0.37	0.19	2.1	1.5
$D_{\rm Li}/10^{-11} {\rm m}^2 {\rm s}^{-1}$	-	0.022	-	0.17
r _{cation} /nm	0.24	0.22	0.20	0.20
r _{anion} /nm	0.22	0.22	0.23	0.26
r _{Li} /nm	-	1.9	-	2.2
Δ	0.44	0.43	0.44	0.40

where

$$M_{\rm mix} = x_{\rm Li} M_{\rm Li} + (1 - x_{\rm Li}) M_{\rm IL}.$$
 (2)

Here, M_{Li} and M_{IL} are the molar masses of LiTFSA and IL, respectively. The Λ values determined are listed in Table 1. For both IL systems, the Λ values decrease by the dissolution of Li⁺ into the ILs. The effect of the dissolution of Li⁺ on the Λ for the C₈dabco⁺-IL system is larger than that for the C₈mim⁺-IL system. The Λ value for the C₈dabco⁺-IL system at $x_{\text{Li}} = 0.1$ was approximately half of the value at $x_{\text{Li}} = 0$. The Walden products ($\eta \Lambda$) of the IL solutions at $x_{\text{Li}} = 0$ and 0.1 are almost unchanged with the dissolution of Li⁺ is due to the decrease in the ion mobilities caused by the increase in the η .

3.2. Chemical shifts

The observed chemical shift (δ_{obs}) on adding Li⁺ into the ILs arises from the changes in both microscopic intermolecular interactions and macroscopic magnetic susceptibility. Thus, we corrected the chemical shifts (δ_{corr}) for the magnetic susceptibility of the sample solution using

$$\delta_{\text{cor}} = \delta_{\text{obs}} - \frac{4\pi}{3} \left(\chi_{\text{v,sam}} - \chi_{\text{v,ref}} \right) \times 10^6, \tag{3}$$

where $\chi_{v,sam}$ and $\chi_{v,ref}$ are the volume magnetic susceptibilities of sample and reference, respectively [32]. The volume magnetic susceptibilities of the sample solutions were determined by the bulbed-capillary external double referencing method before the measurements [33]. In the present analysis, we employed $\chi_{v,sam} = -0.753 \times 10^{-6}$ and -0.773×10^{-6} for the C₈dabco⁺-IL systems at $x_{Li} = 0$ and 0.1, respectively. Those were $\chi_{v,sam} = -0.715 \times 10^{-6}$ and -0.716×10^{-6} for the C_8 mim⁺-IL systems at $x_{Li} = 0$ and 0.1, respectively. The ¹H, ¹³C, and ¹⁵N NMR spectra of the C₈dabco⁺-IL systems at $x_{Li} = 0$ and 0.1, whose horizontal axis of the chemical shift is corrected, are given in Figs. 2-4 together with those of the C₈mim⁺-IL solutions for comparison. All of the ¹H, ¹³C, and ¹⁵N peaks of C₈dabco⁺ shift to the low field when LiTFSA is dissolved into the ILs at $x_{Li} = 0.1$. Importantly, Fig. 4 indicates that the shift of the tertiary N atom at the position 4 within C_8 dabco⁺ ($\delta_{corr} \approx -373.4$ ppm) due to the addition of Li⁺ is more significant than that of the quaternary N⁺ atom at the position 1 ($\delta_{corr} \approx -332.4$ ppm). These results indicate thus that Li^+ in C₈dabco⁺-IL is solvated by the tertiary amine of C₈dabco⁺. On the other hand, Figs. 2-4 show that the shifts of ¹H, ¹³C, and ¹⁵N of C₈mim⁺ for the C₈mim⁺-IL system are not significant. The ¹⁵N peaks of TFSA⁻ in both IL solutions shift to the high field as LiTFSA is dissolved into the ILs. The peak shift to the high field may be due to the interactions between Li⁺ and O atoms of sulfonyl groups in TFSA⁻. The high field shift of the ¹⁵N peak of TFSA⁻ in the C_8 dabco⁺-IL system is smaller than that in the C_8 mim⁺-IL system. This reveals that TFSA⁻ more weakly interacts with Li⁺ in the C₈dabco⁺-IL solution compared to the C₈mim⁺-IL solution because of the strong interaction between C₈dabco⁺ and Li⁺. Fig. 5 shows the ¹⁹F NMR spectra of the C₈dabco⁺- and C₈mim⁺-IL systems at $x_{\text{Li}} = 0$ and 0.1. The ¹⁹F peak of TFSA⁻ in the C₈dabco⁺-IL solution shifts to the low field on adding Li⁺ into the IL while that in the C_8 mim⁺-IL solution shifts to the high field. This can be ascribed to the complicated interactions among cation, anion, and Li⁺. Thus, the inherent cation-anion interactions become stronger in the C₈dabco⁺-IL system by adding Li⁺, probably because of the formation of cation-anion-Li⁺ complex. In contrast, the inherent cation-anion interactions are weakened in the C₈mim⁺-IL system. Fig. 6 shows the ⁷Li NMR spectra of the C_8 dabco⁺- and C_8 mim⁺-IL solutions with LiTFSA. The ⁷Li peak for the C₈dabco⁺-IL solution is observed at the lower field than that for the C₈mim⁺-IL one. This is also attributed to the strong solvation for Li⁺ by C₈dabco⁺ in the C₈dabco⁺-IL solution. As discussed above, the interionic interaction between Li⁺ and TFSA⁻ is weaker in the C₈dabco⁺-IL than the C_8 mim⁺-IL. Consequently, the interactions of Li⁺ with the other ionic species are stronger in the order of C₈dabco⁺ > TFSA⁻ $> C_8 \text{mim}^+$.

3.3. Self-diffusion coefficients

The numerical data of D_{cation} , D_{anion} , and D_{Li} are listed in Table 1. For the IL systems with and without LiTFSA, both D_{cation} and D_{anion} of C_8 dabco-IL are one order of magnitude smaller than those of C_8 mim-IL. The details of the large difference between both systems will be discussed later. In both IL solutions with LiTFSA, the D_{Li} values are obviously smaller compared to those of D_{cation} and D_{anion} , although the size of Li⁺ is much smaller than those of the cations and anion. The smaller D_{Li} than D_{cation} and D_{anion} is often observed in ILs involving TFSA⁻ as a



Fig. 2. ¹H NMR spectra of C_8 dabco⁺- and C_8 mim⁺-IL solutions at $x_{Li} = 0$ and 0.1. The numbers above the peaks give the positions of the hydrogen atoms of the species observed as shown in Fig. 1.



Fig. 3. ¹³C NMR spectra of C_8 dabco⁺- and C_8 mim⁺-IL solutions at $x_{Li} = 0$ and 0.1. The numbers above the peaks give the positions of the carbon atoms of the species observed as shown in Fig. 1.

result of the solvation of Li⁺ by TFSA⁻. The self-diffusion coefficients of the species in the C₈mim⁺-IL system are smaller in the order of $D_{\text{Li}} < D_{\text{anion}} < D_{\text{cation}}$. However, the order of the self-diffusion coefficients for the C₈dabco⁺-IL system is $D_{\text{Li}} < D_{\text{anion}} \approx D_{\text{cation}}$. Thus, the diffusions of the cation and anion are comparable with each other in the C₈dabco⁺-IL system. This is because Li⁺ interacts with C₈dabco⁺ as well as TFSA⁻ in the C₈dabco⁺-IL system, as mentioned above. The Nernst-Einstein deviation parameters (Δ) of the IL solutions at $x_{\text{Li}} = 0$ and 0.1 were obtained from the D_{cation} , D_{anion} , D_{Li} , and Λ values (Table 1) [34]. The Δ values of the present ILs are comparable with those of the other ILs previously reported [34]. The Δ values for both IL systems are less than unity. The Δ values of the IL solutions with LiTFSA at $x_{\text{Li}} = 0.1$ seem to slightly decrease. The smaller Δ values imply the promotion of ionic association in the IL solution with LiTFSA.

To provide interpretation on the molecular scale, further transport studies of various IL solutions with LiTFSA will be required.

The *D* value is often correlated with η and temperature (*T*) according to the Stokes–Einstein equation:

$$D = \frac{k_{\rm B}T}{c\pi r\eta},\tag{4}$$

where $k_{\rm B}$ is the Boltzmann constant and r is the hydrodynamic radius of the diffusing species in the continuous medium. We evaluated the hydrodynamic radius of the diffusing species of the cation, anion, and Li⁺ ($r_{\rm cation}$, $r_{\rm anion}$, and $r_{\rm Li}$, respectively) on the assumption of the stick boundary limit with c = 6. The values of $r_{\rm cation}$, $r_{\rm anion}$, and $r_{\rm Li}$ are given in Table 1. The $r_{\rm cation}$ value for pure C₈dabco⁺-IL is comparable with



Fig. 4. ¹⁵N NMR spectra of (a) cations and (b) anion of C_8 dabco⁺- and C_8 mim⁺-IL solutions with LiTFSA at $x_{Li} = 0$ and 0.1. The numbers above the peaks give the positions of the nitrogen atoms of the species observed as shown in Fig. 1.



Fig. 5. ¹⁹F NMR spectra of C_8 dabco⁺- and C_8 mim⁺-IL solutions with LiTFSA at $x_{Li} = 0$ and 0.1.

that for pure $C_8 \text{mim}^+$ -IL. The r_{anion} values of both ILs agree with each other because of the common anion of TFSA⁻. The possible reason for the comparable r_{cation} values for the ILs is attributed to the common octyl chain of C₈dabco⁺ and C₈mim⁺, despite of the different sizes of the charged moieties. Nevertheless, the D_{cation} and D_{anion} values for C₈dabco⁺-IL are much smaller than those for C₈mim⁺-IL. Hence, the slower diffusion motions of the cation and the anion in the former than those in the latter are due primarily to the different η between the ILs. According to the literature [9], the radii of non-polymer species where a Li⁺ is solvated by two and four TFSA⁻ are 0.6 and 0.8 nm, respectively. The r_{Li} values for both IL solutions in the present study are larger than that of the non-polymer form in the subnanometer range [9]. It is suggested thus that Li⁺, cation, and anion form the complex polymers in both IL systems. Therefore, both D_{Li} values of the IL solutions may correspond to the diffusion motion of the polymer including Li^+ . The slight increase in the r_{anion} of the C_8mim^+ -IL system on adding Li⁺ suggests that Li⁺-TFSA⁻ polymers with several Li⁺ may be produced in the C₈mim⁺-IL solution. In the C₈dabco⁺-IL solution, Li⁺-C₈dabco⁺-TFSA⁻ polymers may be formed due to the coordination ability of the cation. This is corroborated from the different sizes $(r_{\rm Li} \approx 1.9 \text{ nm and } r_{\rm Li} \approx 2.2 \text{ nm, respectively})$ of the polymers in the C₈dabco⁺-IL and C₈mim⁺-IL solutions.



Fig. 6. ⁷Li NMR spectra of C₈dabco⁺- and C₈mim⁺-IL solutions with LiTFSA at $x_{Li} = 0.1$.

3.4. Relaxation times and correlation times

The values of $T_{1,\text{Li}}$ at two different magnetic field strengths of 9.4 and 14.1 T are listed in Table 2. In each of IL system, the $T_{1,\text{Li}}$ value at 9.4 T is significantly shorter than that at 14.1 T. This means that the extreme narrowing condition $(2\pi\nu\tau_c \ll 1)$ cannot be satisfied for the relaxation of ⁷Li nucleus in the IL solutions. The ⁷Li nucleus with the spin quantum number of I = 3/2 relaxes through the quadrupolar interaction. Hence, the observed $T_{1,\text{Li}}$ under no extreme narrowing condition is related to the correlation time ($\tau_{c,\text{Li}}$) as a function of resonance frequency (ν) [35]:

$$\frac{1}{T_{1,\text{Li}}} = A \left(\frac{\tau_{\text{c,Li}}}{1 + 4\pi^2 v^2 \tau_{\text{c,Li}}^2} + \frac{4\tau_{\text{c,Li}}}{1 + 16\pi^2 v^2 \tau_{\text{c,Li}}^2} \right), \tag{5}$$

where *A* is a constant enclosing a quadrupole coupling constant, dependent on the sample system. Assuming that the relaxation of ⁷Li predominantly takes place through the quadrupolar mechanism, we estimated the $\tau_{c,Li}$ value from a pair of the $T_{1,Li}$ at 9.4 and 14.1 T. As shown in Table 2, the $\tau_{c,Li}$ values for both IL solutions are in the subnanosecond range. This agrees with the $\tau_{c,Li}$ range for 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide [20]. Hayamizu et al. [20] interpreted the $\tau_{c,Li}$ in ILs as the correlation time of the translational motion by jumping of Li⁺ rather than tumbling motion. The $\tau_{c,Li}$ values arise from the time of the jump motion of Li⁺ from the solvating site to the other site. The $\tau_{c,Li}$ value for the C₈dabco⁺-IL solution is obviously larger than that for the C₈dabco⁺-IL solution than that in the C₈mim⁺-IL one.

3.5. Solvation structure and dynamics of Li⁺

As discussed on the NMR spectra (Figs. 2–6), Li^+ in the C₈dabco⁺-IL solution is solvated by C₈dabco⁺ as well as TFSA⁻, whereas Li⁺ in the C₈mim⁺-IL solution is solvated by TFSA⁻, but not by C₈mim⁺. For both IL solutions, the smaller D_{Li} values than the D_{cation} and D_{anion} ones show that the diffusion motion of Li⁺ is not faster than those of the cation and the anion. The r_{Li} value for the C₈dabco⁺-IL solution is much smaller than that of the C₈mim⁺-IL solution, whereas the $\tau_{c,Li}$ for the former is longer than the latter. The longer $\tau_{c,li}$ for the C₈dabco⁺-IL solution suggests the stronger interaction of Li⁺ with C_8 dabco⁺ and TFSA⁻ in the C_8 dabco⁺-IL solution than the interaction with TFSA⁻ in the C₈mim⁺-IL solution. Thus, the jump motion of Li⁺ is more retarded in the C₈dabco⁺-IL solution than the C₈mim⁺-IL solution. The D_{Ii} value of the C₈dabco⁺-IL solution is given by the diffusion motion of the Li⁺-C₈dabco⁺-TFSA⁻ polymer. Li⁺ in the C₈dabco⁺-IL solution may jump from one site to the other site in the Li⁺-C₈dabco⁺-TFSA⁻ polymer. The smaller D_{Ii} than D_{cation} and D_{anion} may mainly arise from that Li⁺ jumps inside the polymer, but does not from the polymer to the other one. In contrast, the jump of Li⁺ occurs among the looser Li⁺-TFSA⁻ polymers in the C₈mim⁺-IL solution. This results in the shorter $au_{c,Li}$ for the C₈mim⁺-IL solution than that for the C_8 dabco⁺-IL solution.

4. Conclusion

To clarify the solvation structure and dynamics of Li^+ in the Lewisbasic C₈dabco-IL, we determined NMR chemical shifts, longitudinal

Table 2

⁷Li longitudinal relaxation times ($T_{1,Li}$) and correlation times ($\tau_{c,Li}$) of Li⁺ in C₈dabco⁺- and C₈mim⁺-IL solutions with LiTFSA at $x_{Li} = 0.1$ and 313.2 K.

IL	T _{1,Li} /s		$ au_{ m c,Li}/ m ns$
	9.4 T	14.1 T	
[C ₈ dabco][TFSA]	0.353	0.588	0.719
[C ₈ mim][TFSA]	0.371	0.548	0.490

relaxation times, and self-diffusion coefficients in the C₈dabco⁺-IL solution. These results were compared with those in the C₈mim⁺-IL solution. We reached the conclusion that Li⁺ in the C₈dabco⁺-IL solution interacts with both C₈dabco⁺ and TFSA⁻. In the C₈mim⁺-IL solution, Li⁺ diffuses as the Li⁺-TFSA⁻ polymer. Li⁺ jumps among the bridging TFSA⁻ in the polymers. In the C₈dabco⁺-IL solution, the diffusion of Li⁺ takes place as the Li⁺-C₈dabco⁺-TFSA⁻ polymer. Li⁺ may jump from the site to the other in the polymer.

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