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# Study of ion dynamics of LiI·6H<sub>2</sub>O in the supercooled liquid state using NMR spectroscopy and ionic conductivity measurements



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ARTICLE INFO	A B S T R A C T			
<i>Keywords:</i> Diffusion Ion dynamics Glass transition	Ion dynamics in the liquid and supercooled liquid state of LiI- $6H_2O$ were studied by nuclear magnetic resonance (NMR) spectroscopy and ionic conductivity measurements. The self-diffusion coefficients of the water molecules and lithium ions were measured by <sup>1</sup> H and <sup>7</sup> Li pulsed gradient spin echo NMR (PGSE-NMR). The temperature dependences of the DC ionic conductivity and diffusion coefficients of lithium ions and water molecules were well-fitted by the Vogel-Tamman-Fulcher (VTF) law, similar to those of the LiCl- $RH_2O$ system. The conductivity and lithium diffusion coefficients of the LiI- $6H_2O$ system were more than twice those of LiCl- $7H_2O$ in the supercooled liquid state below 200 K, which could be attributed to the larger size of the iodide anions than that of chloride anions. The temperature dependence of the correlation times calculated from NMR $T_1$ relaxation deviated from the VTF law at low temperatures because of the local orientational fluctuation of the water molecules			

## 1. Introduction

Ionic transport in the supercooled liquid state has been investigated extensively over recent decades because it is a good indication of slow dynamics in glass-forming systems [1] and the performance of devices such as lithium ion batteries and fuel cells [2,3]. It is well known that the viscosity  $\eta$  of a supercooled liquid increases drastically with decreasing temperature close to the glass transition temperature,  $T_g$ , which is expressed by the Vogel-Tamman-Fulcher (VTF) equation:

$$\eta = \eta_0 \exp\left(\frac{B}{T - T_0}\right),\tag{1}$$

where  $\eta_0$ , *B*, and  $T_0 < T_g$  are the parameters of the VTF equation. Corresponding to this equation, the ionic conductivity  $\sigma$  also follows the same VTF form as follows:

$$\sigma = \sigma_0 \exp\left(\frac{-B}{T - T_0}\right),\tag{2}$$

where  $\sigma_0$ , *B*, and  $T_0 < T_g$  are the parameters. If Eqs. (1) and (2) have the same *B* and  $T_0$  parameters, then their product is independent of the temperature *T*, as follows:

$$\sigma\eta = \sigma_0 \eta_0 = const. \tag{3}$$

This is a natural consequence of the so-called Walden rule

 $\Lambda \eta = const.$  [4], where  $\Lambda$  is the molar conductivity. Eq. (3) suggests a drastic decrease in conductivity approaching  $T_0$ . This means that the translational motion of the charge carrier ions is strongly coupled with the macroscopic mechanical relaxation process ( $\alpha$ -process); these systems were named as coupled systems by Angell [5]. However, the ionic conductivity  $\sigma$  is sometimes found to be much larger than the value expected from Eq. (3), which is designated as a strongly decoupled system [5-7]. A typical example is the so-called superionic conductor glass AgI-Ag<sub>2</sub>MoO<sub>4</sub>, where the transport of silver ions is decoupled from the viscosity and manifests as its very high conductivity of  $10^{-3}$  S/cm at  $T_{\sigma}$  [7,8]. If a lithium ion is decoupled from the viscosity in the supercooled liquid state, then the fast lithium ion motion will be sustained and impart high lithium ion conductivity in the glassy state, which would be useful for battery applications. Unfortunately, however, the supercooled liquid state of lithium salt solutions is mostly a strongly coupled system [5,6,9].

In the case of the LiCl·H<sub>2</sub>O system, the structure and dynamics in the supercooled liquid state have been investigated extensively over recent decades, which is partly related to the so-called mode-coupling approach to glass transition [10] and also related to the glass transition of H<sub>2</sub>O itself [11,12]. In particular, the concentration of LiCl·6H<sub>2</sub>O (molar ratio of LiCl:H<sub>2</sub>O is 1:6), which is close to the eutectic composition, is known to be very stable in the supercooled liquid state without crystallization even under slow cooling conditions [13–15]. Many structural

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analyses have been conducted using X-ray diffraction [16,17], neutron scattering [13,16–22], and computer simulations [23]. Several studies on such systems have reported on the slow dynamics, viscosity [24], ionic conductivity [25–27], and diffusion coefficients [28–30]. In the case of short time-scale dynamics, Raman [31] and Brillouin scatterings [32,33], quasi-elastic neutron scattering (QENS) [34,35], and NMR relaxation [28,29,36] are known.

All these experiments indicate that the lithium ions are strongly coordinated by the surrounding oxygen atoms of water molecules, which also form a hydrogen bonding network with other water molecules. The lithium ions are embedded in the long-range network structure such as -H<sub>2</sub>O-Li-H<sub>2</sub>O-Li-H<sub>2</sub>O-Li-H<sub>2</sub>O; note that the actual coordination number of water around a lithium is 4 or 5, which gives a three-dimensional network. Thus, the lithium ion can be regarded as a member of the abovementioned network in LiCl·6H<sub>2</sub>O glass, although LiCl weakens the hydrogen bond network of water [16,37]. It is quite different from conventional inorganic glasses such as Li<sub>2</sub>O·SiO<sub>2</sub>, where the glass network is formed only by Si-O covalent bonds. The lithium ions located near the oxides are decoupled from the network and can migrate along the network and result in a rather high lithium ion conductivity; it is considerably more prominent in Li2SSiS2 glasses whose lithium conductivity is  $10^{-4}$  S/cm at room temperature. In the case of the LiCl<sup>6</sup>H<sub>2</sub>O system, because this network structure contains lithium ions, the ionic conductivity decreases with decreasing temperature and is inversely proportional to the viscosity. Therefore, the system for which Eq. (3) is applicable over a wide temperature range is categorized as a coupling system.

It should be noted, however, that most of the lithium ions are involved in the network structure whose dynamics are the same as slow  $\alpha$ relaxation, some of which may move locally in restricted regions and contribute to the so-called  $\beta$ -relaxation [38,39] that is detected in optical Brillouin scattering [32,33], dielectric [40,41], and NMR [42] spectroscopies.

Only a few challenges have been known regarding the decoupling of lithium motion from the liquid  $\alpha$ -relaxation. Cooper and Angell [43] reported such a possibility in the mixture LiI-(MeOEt)EtMe<sub>2</sub>NI. A Japanese patent describes an mixture containing LiI, 85LiI-10TMAI (Tetramethylammonium iodide) ·5EQI (1-Ethylquinaldinium iodide), which exhibits a high ionic conductivity of  $10^{-6}$  S/cm even at  $T_g$ , and can be considered as a decoupled lithium salt system [44,45]. In these reports, it is discussed that the larger size of the iodide anion plays an important role in enhancing the lithium ion motion owing to the packing gap among the iodides, small surface charge, and large polarizability. Based on these reports, it is anticipated that even in the aqueous solutions of the LiCl·H<sub>2</sub>O system, which are known as a strongly coupled systems, replacing the chloride by iodide may reduce the coupling and enhance the mobility of lithium ions.

Surprisingly, however, only a few reports have been published on the structure and dynamics of LiI·H<sub>2</sub>O systems [34,46–49]. No reports are available on the glass-forming region or the ionic conductivity in the supercooled liquid state of the LiI·H<sub>2</sub>O system, although LiI itself is known as a fairly good ionic conductor of  $2.8 \times 10^{-8}$  S/cm at 25 °C [50] for application in a solid battery for cardiac pacemakers [51]. LiI·H<sub>2</sub>O is also known as a perovskite-type solid electrolyte with a lithium ion conductivity of  $6.6 \times 10^{-6}$  S/cm at room temperature [50]. Moreover, when LiI is hybridized with insulating oxides (e.g., Al<sub>2</sub>O<sub>3</sub>) at the nanoscale, its conductivity increases up to  $10^{-4}$  S/cm [52,53].

Therefore, in this study, we first investigated the stability region of the supercooled liquid state and glass transition temperatures in a LiIrRH<sub>2</sub>O (R = 4–10) system using differential scanning calorimetry (DSC) analysis. Then, the best composition (LiI-6H<sub>2</sub>O) was selected for further study. Further, the ionic AC conductivity and NMR diffusion coefficients of <sup>7</sup>Li and <sup>1</sup>H nuclei as well as relaxation time  $T_1$  were measured for the LiI-6H<sub>2</sub>O solution. These results were compared to those of the LiCl-6H<sub>2</sub>O system, and the effect of the halide ion was discussed.

#### 2. Experimental

Appropriate amounts of LiI (High purity Chemical Co., 99.9% up) were dissolved in deionized water to obtain various compositions, represented as LiI- $RH_2O$ , where R = 4-10 refers to the number of moles of water per mole of salt. To determine the stability region of the supercooled liquid state, we measured the DSC thermograms using EXSTAR DSC6000 (SII Co.). Each prepared sample solution was sealed in an aluminum pan for DSC. Initially, the prepared sample solution was cooled from room temperature to 123 K using cold nitrogen gas at an estimated cooling rate of 30 K/min or less. The DSC scan was started from 123 K to 323 K at a heating rate of 10 K/min.

The ionic conductivity was measured by the AC impedance method using a Solartron 1260 impedance gain phase analyzer with a current amplifier in the frequency range from 1 Hz to 500 kHz. Near the room temperature between 223 K and 353 K, a conventional home-made parallel plate cell was used, which had an electrode area of  $0.0314 \text{ cm}^2$  and electrode separation of 9.4 mm. The temperature was controlled by a thermostatic chamber (ESPEC SU-661). Below 223 K, it was difficult to obtain reliable data using the conventional cell because the conductivity became too small in this region. Therefore, another parallel plate cell was used at temperatures below 223 K down to 43 K, which had a large electrode area of 11.3 cm<sup>2</sup> and a separation gap of 2.0 mm (Hewlett-Packard 16452A liquid test fixture). The temperature of the cell was controlled from 143 K to 223 K in a home-made cryostat using hydrofluoroether as the cooling medium.

NMR measurements were conducted using a Bruker Avance III NMR spectrometer with a superconducting magnet of 11.7 Tesla. The <sup>1</sup>H and <sup>7</sup>Li NMR spectra were measured at the Larmor frequency of  $f_{1H} = 500$  MHz for <sup>1</sup>H and  $f_{7Li} = 194$  MHz for <sup>7</sup>Li. Self-diffusion coefficients and NMR relaxation times  $T_1$  were measured using a broadband multi-nuclear probe for a 5 mm tube, which was equipped with a gradient unit for diffusion measurements.

Diffusion coefficients were measured by the pulsed gradient spin echo (PGSE) method with sine-shaped gradient pulses. A 13-interval bipolar stimulated echo pulse sequence [54] was applied from 170.0 K to 300.0 K. To avoid possible convection effects at high temperatures, a double sequence [55] was added in the temperature range of 312.4–353.3 K. Diffusion coefficients were calculated using Eq. (4) as follows:

$$I = I_0 \exp\left[-D(\gamma \delta^* g)^2 \left(\Delta^* - \frac{1}{3}\delta^*\right)\right]$$
(4)

where  $\gamma$  and g are the gyro magnetic ratio and effective gradient pulse strength, respectively; effective gradient pulse strength in sine-shape gradient pulse is maximum value of gradient multiplied by  $2/\pi$ ,  $\Delta^* = \Delta + \tau 3/2 + \delta/2$  and  $\delta^* = 2\delta$ ;  $\tau$  is the interval between  $\pi/2$  and the next  $\pi$  pulse,  $\Delta$  is the interval between the second and third  $\pi/2$  pulses, and  $\delta$  is the gradient pulse length [54]. The NMR echo signal was recorded for each variable gradient pulse strength g. The appropriate  $\delta$  value was selected from 1 ms to 10 ms for <sup>1</sup>H and from 2 ms to 20 ms for <sup>7</sup>Li depending on the temperature.  $\tau$  was chosen as  $\delta + 0.2$  ms and  $\Delta^*$  was fixed to 500 ms in all experiments. The relaxation times  $T_1$  were measured by the conventional inversion recovery method, where the 90° pulse was 17.5 µs for <sup>1</sup>H and 10 µs for <sup>7</sup>Li. To accurately evaluate the sample temperature, a fiber-optic thermometer (Anritu Meter) was inserted into the sample in the NMR tube. The accuracy of the experimental temperature value of NMR measurements was improved to  $\pm 0.5$  K.

## 3. Results

#### 3.1. Differential scanning calorimetric analysis

The DSC thermograms of LiI-RH<sub>2</sub>O are shown in Fig. 1, which were obtained at an elevated temperature of 10 K/min. Each sample showed a step at  $\sim$ 143 K corresponding to the glass transition temperature  $T_{e}$ .



Fig. 1. Differential scanning calorimetry (DSC) thermograms of the Lil-RH<sub>2</sub>O systems, where the arrows indicate the glass transition temperature,  $T_{e}$ .

Exothermic peaks observed at ~100–120 K for the LiI- $RH_2O$  samples, where R = 4, 4.5, 5, 7.5, and 8, corresponded to crystallization, and the endothermic peaks represented melting. No exothermic or endothermic peaks were observed in the thermograms of samples with R = 6, which suggested that the supercooled liquid state was very stable at this composition.

The phase diagram of LiIrRH<sub>2</sub>O determined by the DSC measurements is shown in Fig. 2. The melting point of lithium trihydrate is known to be 346 K [56]. The glass transition temperatures were ~143 K, independent of the composition in the range of R = 4–10. The solid–liquid coexistence curves were determined from the observed melting points in  $R \leq 5$  and  $R \geq 7.5$ , although no crystallization or melting points were observed in the composition range of R = 5.5–7 because of the large stability of the supercooled liquid state. The melting point shown in Fig. 2 had a minimum at  $R \sim 6$ , which suggested that the eutectic point was at  $R \sim 6$  and 193 K. The eutectic composition at  $R \sim 6$  was similar to that of the LiCl·H<sub>2</sub>O and LiBr·H<sub>2</sub>O systems [13,15,57].

#### 3.2. NMR diffusion coefficients

Fig. 3(a) shows the temperature dependence of the diffusion coefficients of  ${}^{1}$ H and  ${}^{7}$ Li nuclei measured by PGSE-NMR, both of which could be fitted by the VTF equation,



**Fig. 2.** Phase diagram of LiI-*R*H<sub>2</sub>O for R = 4-10. Melting point of LiI-3H<sub>2</sub>O was obtained from reference [56]. The glass transition temperature ( $T_g$ ) and melting temperature ( $T_{mp}$ ) are shown.

$$D = D_0 \exp\left(\frac{-B}{T - T_0}\right).$$
(5)

The fitting parameters were evaluated to be  $D_0 = 3.0 \times 10^{-8} \text{ m}^2/\text{s}$ , B = 531 K,  $T_0 = 133 \text{ K}$  for proton and  $D_0 = 2.3 \times 10^{-8} \text{ m}^2/\text{s}$ ,



Fig. 3a. Temperature dependence of the diffusion coefficients of  ${}^{1}$ H and  ${}^{7}$ Li nuclei. The results were fitted to the VTF equation.



**Fig. 3b.** Temperature dependence of the diffusion coefficients. The broken lines are the VTF-fitting results of LiI-7 $H_2O$  for <sup>1</sup>H (blue) and <sup>7</sup>Li (red) from reference [28].

Table 1 VTF parameters for transport coefficients of LiI-6H<sub>2</sub>O, LiCl-7H<sub>2</sub>O [27,28] and LiCl-6H<sub>2</sub>O [29].

Property	X <sub>0</sub>	B/K	<i>T</i> <sub>0</sub> /K		
Lil·6H <sub>2</sub> O					
$D_{\rm H}/m^2 s^{-1}$	$3.0 \times 10^{-8}$	531	133		
$D_{Li}/m^{2}s^{-1}$	$2.3 \times 10^{-8}$	578	133		
$\sigma/\Omega^{-1}$ cm <sup>-1</sup>	$1.3 \times 10^{-8}$	432	133	(fit 1 in Fig. 6a)	
$\sigma/\Omega^{-1} \text{cm}^{-1}$	$4.5 \times 10^{-8}$	687	115	(fit 2 in Fig. 6a)	
LiCl-7H <sub>2</sub> O[27.28]					
$D_{\rm H}/m^2 s^{-1}$	$1.02 \times 10^{-8}$	870	114		
$D_{Li}/m^2 s^{-1}$	$1.02 \times 10^{-8}$	911	116		
$\sigma T/\Omega^{-1}m^{-1}K$	$7.785 \times 10^{-8}$	885	118		
LiCl·6H <sub>2</sub> O[29] $D_{H}/m^{2}s^{-1}$	$3.55 \times 10^{-8}$	751	113		

B = 578 K,  $T_0 = 133$  K for lithium, which are listed in Table 1. The ratio of the two diffusion coefficients  $D_{H}^1/D_{Li}^7$  is shown in Fig. 4, which was ~1.7 at room temperature and increased at low temperatures. A higher diffusion coefficient of the solvent  $D_{H}^1$  than the salt  $D_{Li}^7$  is commonly observed in aqueous and non-aqueous lithium salt solutions



Fig. 4. Temperature dependence of the ratio of diffusion coefficients  $D_{1H}/D_{7Li}$ . The broken line corresponds to Eq. (8).

[28,29,58,59]. The  $D_{\rm H}^1 / D_{\rm Li}^7$  ratio of 1.7 at room temperature increased to 2.5 at 188 K; this tendency is similar to that of the LiCl<sup>.</sup>7H<sub>2</sub>O solution [28]. A systematic difference was found between the diffusion coefficients of LiCl<sup>.7</sup>H<sub>2</sub>O and Lil<sup>.6</sup>H<sub>2</sub>O, especially at low temperatures. The  $D_{\rm Li}^7$  value of LiCl·7H<sub>2</sub>O was almost the same as that of LiI·6H<sub>2</sub>O within 5% at 300 K; however, the value for LiI·6H<sub>2</sub>O was 2.3 times that of LiCl $^{7}$ H<sub>2</sub>O at 188 K, as shown in Fig. 3(b). Diffusion coefficient of <sup>1</sup>H in LiI·6H<sub>2</sub>O is half of that in pure H<sub>2</sub>O [60] at around room temperature because adding the salt increases the viscosity. However, <sup>1</sup>H diffusion coefficient of <sup>1</sup>H diffusion coefficient in pure water approaches that in LiI-6H<sub>2</sub>O with decreasing temperature, and the two values become almost the same at 243 K. Comparing the two values at temperatures below 243 K is of interest; however, measuring the diffusion coefficient of pure water at lower temperatures is limited due to stability of the super-cooled liquid state. Therefore, we could not compare <sup>1</sup>H diffusion coefficients in LiI- $6H_2O$  and pure water at temperatures below 237.8 K.

# 3.3. NMR $T_1$ relaxation

The temperature dependences of the longitudinal relaxation time  $T_1$  of <sup>1</sup>H and <sup>7</sup>Li nuclei are shown in Fig. 5. The  $T_1$  of each nucleus showed a minimum where the NMR frequency was equal to the inverse of the correlation time of the nucleus dynamics. This temperature dependence of  $T_1$  is very similar to those reported for concentrated aqueous



**Fig. 5.** Temperature dependence of the  $T_1$  relaxation times of <sup>1</sup>H and <sup>7</sup>Li.



**Fig. 6a.** Temperature dependence of DC conductivity. Experimental results from AC impedance ( $\sigma$ ) and calculated from <sup>7</sup>Li diffusion coefficient ( $\sigma$ <sub>DLi</sub>) are shown. The solid and broken lines correspond to the fitting to VTF law at high (fit 1) and low (fit 2) temperatures, respectively.

solutions of LiCl [28,29,61,62] and LiI [48]. The correlation time was evaluated from the temperature dependence of  $T_1$ , which will be discussed in detail in Section 4.

## 3.4. DC conductivity

Fig. 6(a) shows the temperature dependence of the DC conductivity of LiI·6H<sub>2</sub>O, which was determined from the AC impedance experiments. In this figure, the calculated values of  $\sigma_{DLi}$  from the diffusion coefficients of <sup>7</sup>Li are also shown, which were in fairly good agreement with the observed conductivity, as will be discussed in Section 4. The observed temperature dependence of the DC conductivity was fitted well by the VTF Eq. (2), where the parameters were evaluated as  $\sigma_0 = 1.3$  S/cm, B = 432 K, and  $T_0 = 133$  K, as shown in Table 1. However, it was evident in Fig. 6(a) that the experimental values deviated from the VTF curve at temperatures below 166 K, which is near the glass transition temperature  $T_g = 143$  K. A similar deviation of both conductivity and viscosity from the VTF law at temperatures below  $T_g$  + 50 K is already known in various glass-forming systems [63,64]. To compare with the previously reported data [26,27], another VTF fitting was performed focusing on the low-temperature region, which gave  $\sigma_0 = 4.5$  S/cm, B = 687 K, and  $T_0 = 115$  K. These parameters fit better at low temperatures, as shown in Fig. 6(a) by a dotted curve, despite some deviation at high temperatures.

The observed conductivity values of LiI·6H<sub>2</sub>O were compared with those of LiCl·6H<sub>2</sub>O and LiCl·7H<sub>2</sub>O in Fig. 6(b). Moynihan et al. have reported the ionic conductivity of LiCl·RH<sub>2</sub>O for R = 5.34 and R = 6.72 at ~173 K [25]. We calculated the conductivity of R = 6 and 7 by linear interpolation for each temperature, as shown by the circles in Fig. 6(b). The conductivity of LiCl·7H<sub>2</sub>O was merely 1.3 times larger than that of LiCl·6H<sub>2</sub>O. This suggested that the influence of the concentration difference between six and seven H<sub>2</sub>O is rather weak. Cramer et al. have shown the VTF fitting of conductivity of LiCl·7H<sub>2</sub>O [27], which corresponds to the blue curve in Fig. 6(b). The observed DC conductivity of Lil·6H<sub>2</sub>O was about twice that of LiCl·6H<sub>2</sub>O at ~173 K. This relation agrees well with the experimental results of the diffusion coefficients shown in Fig. 3(b).

#### 3.5. Frequency dependence of the conductivity

It is well known that the ionic conductivity in supercooled liquids or glassy states depends on the observed frequency [7,65]. Fig. 7 shows



**Fig. 6b.** Temperature dependence of DC conductivity in the low-temperature region. Plots for LiI-6H<sub>2</sub>O, LiCl-6H<sub>2</sub>O (\*1 [25]), LiCl-7H<sub>2</sub>O (\*1 [25] and \*2 [27]) are shown.  $T_{g,I}$  and  $T_{g,CI}$  refer to the glass transition temperatures of LiI-6H<sub>2</sub>O and LiCl-7H<sub>2</sub>O, respectively.



**Fig. 7.** Frequency dependence of ionic conductivities close to the glass transition temperature. The plots (bottom to top, respectively) correspond to temperatures 143.4, 145.4, 150.6, 155.7, 160.8, and 165.9 K. The results were fitted using Eq. (6).

the frequency dependence of the real part of conductivity close to the glass transition temperature. A behavior typical of ionic conductors was observed; that is, the conductivity increased with increasing frequency at low temperatures (Eq. (6)).

$$\sigma[i\omega] = \sigma_{dc} \{ 1 + (i\omega\tau_{\sigma})^n \}.$$
(6)

Here,  $\sigma_{dc}$  is the DC conductivity,  $\tau_{\sigma}$  is the conductivity relaxation time, and the exponent *n* is the distribution parameter, which is estimated to be n = 0.65. Although the nearly constant-loss [66] term, *Cw*, is effective at higher frequencies, it was not significant here. The fitting results are shown as the solid curves in Fig. 7, and the conductivity relaxation times  $\tau_{\sigma}$  are shown in Fig. 8 by black squares.

## 4. Discussions

#### 4.1. Glass-forming region and structure

The observed glass transition temperature of LiI-6H<sub>2</sub>O (143 K) is only 5 K higher than that of LiCl-6H<sub>2</sub>O (138 K) [13,14]. Thus, there is no significant influence of the anion in these systems. The glass transition temperature,  $T_{g_2}$  of pure water is reported to be 136 K [12,67],



Fig. 8. Temperature dependence of correlation time calculated from ionic conductivities and NMR  $T_1$  relaxation.

and those of dilute LiCl·*R*H<sub>2</sub>O solutions range from 132 to 129 K [14]. With increasing salt concentration, the  $T_g$  suddenly changes from 132 K to 142 K at R = 20. Above this concentration, all the water molecules are thought to be involved in the hydration of the salts, and the cage structure of pure water is diminished. X-ray and neutron diffraction analyses suggest that the salt ions act as a structure breaker [16,17] and the tetrahedral hydrogen bond network of water diminishes with increasing salt concentration, which disappears at a concentration of R = 10 [17]. From this information on LiCl·*R*H<sub>2</sub>O systems, it is clear that the hydrogen-bonded water molecules, as they exist in pure water, do not remain in LiI·6H<sub>2</sub>O.

# 4.2. Temperature dependence of the diffusion coefficients

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As shown in Section 3.2 and in Fig. 3(b) and Fig. 4, the diffusion coefficients of the lithium ions,  $D_{\text{Li}}$ , and protons (water),  $D_{\text{H}}$ , follow a similar VTF dependence, although the latter is always larger than the former, especially at low temperatures. To address this difference, we started from the Stokes-Einstein law:

$$D_i = \frac{k_B T}{6\pi\eta r_i},\tag{7}$$

where  $r_i$  is the radius of species *i* and  $\eta$  is the viscosity of the liquid. The effective radius (Stokes radius) of the diffusive ion in solution included not only the ion itself but also the solvated molecules. The effective radius of a Li<sup>+</sup> ion in aqueous solution is reported to be 0.239 nm by the classical Stokes law under the stick condition [68]. The value of  $D_{1H}/D_{7Li}$  calculated from Eq. (7) using  $r_{Li+} = 0.239$  nm and  $r_{water} = 0.139$  nm [69] was 1.72. This value was in good agreement with the experimental result near the room temperature, as shown in Fig. 4. The *B* parameter of the VTF equation for <sup>1</sup>H (531 K) was smaller than that of <sup>7</sup>Li (578 K). From a simple free-volume theory, the *B* parameter of the vTF equation was proportional to the effective volume ratio between the mobile ions and surrounding matrix species [70]. Thus, the smaller *B* value of  $D_{1H}$  compared to that of  $D_{7Li}$  was attributed to the larger size of the solvated lithium ions than that of water molecules, which is in accordance with the above discussion of Stokes law.

However, the origin of the temperature dependence of  $D_{1H}/D_{7Li}$  is rather new and unclear. From the Stokes law (Eq. (7)), it may be related to the temperature dependence of the effective radius and/or coordination number. Feiweier et al. reported a similar trend in LiCl·7H<sub>2</sub>O and pointed out a possible "decoupling of the proton motion" from the matrix [28]. They also revealed that the diffusion coefficient of <sup>1</sup>H at low temperature was higher than that expected from its viscosity. The decoupling of the smaller species from the matrix is well known in the field of superionic conductor glasses, and can be analyzed by the excess free-volume theory [70], which predicts that smaller species are decoupled from the matrix of larger species; the  $D_{1H}/D_{7Li}$  ratio is proportional to the decoupling index,  $R_r$ , which is expressed as follows [70]:

$$R_{\tau} \propto \frac{\tau_{0Li}}{\tau_{0w}} \exp\left[\frac{b_{Li}/b_w}{\Delta\alpha(T-T_0)+\delta}\right],\tag{8}$$

where  $b_{\rm Li} = 4/3\pi r_{\rm Li}^3$ ,  $b_{\rm w} = 4/3\pi r_{\rm water}^3$ ,  $\Delta \alpha$  is the thermal expansion coefficient of the free volume, and  $\delta$  is the remaining excess free volume. The fitting of Eq. (8) to the experiments is shown by the dashed curve in Fig. 4, where the following parameters are used:  $\tau_{\rm 0Li}/\tau_{\rm 0w} = 1.25$ ,  $\Delta \alpha = 0.13$ ,  $\delta = 0$ , and  $b_{\rm Li}$  and  $b_{\rm w}$  are calculated from the effective radius given above as  $r_{\rm Li} = 0.239$  nm and  $r_{\rm w} = 0.139$  nm.

As shown in Figs. 3(b) and 6(b), a higher mobility of LiI-6H<sub>2</sub>O than that of the LiCl system was observed at low temperature. The difference increased with decreasing temperature, which suggests quite a large difference at  $T_g$ , as outlined in the Introduction. This is probably due to the larger size of the iodide compared to that of chloride; i.e., the larger polarizability and smaller surface charge of the iodide anion reduced the Coulombic binding energy to the lithium ions.

## 4.3. Ionic conductivity and diffusion coefficient

As shown in Fig. 6(a), the temperature dependence of the DC conductivity also followed the VTF Eq. (2), the parameters of which are shown in Table 1. These parameters are very close to those evaluated from the diffusion coefficient  $D_{\rm Li}$  of lithium ions. This is a simple consequence of the Nernst-Einstein law, which is given as follows:

$$\sigma = \sum_{i} \frac{n_{i} q_{i}^{2}}{k_{B} T} D_{i}.$$
(9)

Here, *n* is the number density of species *i* and *q<sub>i</sub>* is its charge, and *D<sub>i</sub>* is the diffusion coefficient. The charge carriers of this system are lithium and iodide ions. However, the diffusion measurement of the iodide anion by PGSE-NMR is quite difficult because of its extremely short *T*<sub>2</sub> relaxation time. Therefore, we tentatively estimated the partial conductivity from the diffusion coefficient of only the lithium cation, whose number density was  $n_{\text{Li}} = 4.1 \times 10^{27} \text{ m}^{-3}$ . The partial conductivity calculated from the diffusion coefficient of lithium ions was close to the observed total conductivity, as shown in Fig. 6(a), although a deviation was observed at higher temperatures. This deviation cannot be attributed to the iodide ions that were neglected, as this would further increase the calculated *s* values and the deviation.

The deviation from the Nernst-Einstein law, in particular the lower values of observed conductivity, has been known for more than half a century in aqueous electrolyte solutions [71,72] and recently in non-aqueous solutions as well [73–75]. This deviation has been attributed to the association of the cations and anions to form ion pairs in solution. The paired cations and anions contribute to each diffusivity, although they do not contribute to the ionic conductivity because their charges are canceled. The tendency of ion association is characterized by the ratio of the electrostatic potential energy of associated paired ions and thermal energy, which is known as the Bjerrum parameter [76]. Fuoss et al. summarized the association constant for various salts in aqueous solutions from the concentration dependence of molar conductivity [71,72]. These phenomena are discussed in consideration of the possible structure of the direct ion pairs and the indirect association of ions with the intermediate water molecules [77].

As can be seen in Fig. 6(a), the deviation was larger at high temperatures, which suggests that there was more ion association at higher temperatures than at lower temperatures. Similar results have been reported in different solutions based on NMR diffusion data [58] and the concentration dependence of the conductivity [78,79]. This

tendency may be explained by the temperature dependence of the dielectric constant and/or the entropy effect [80]. Fuoss et al. measured the ionic association in a water-dioxane binary solution [71,76] and found that the association increased with decreasing solvent dielectric constant. Therefore, the association increased because the water dielectric constant decreased with increasing temperature. The other possibility is called an "entropy-driven association", where the structure of the ionic solution is considered as an ordered (low entropy) network of hydrogen bonds and coordinating bonds between the solute (water molecules) and both ions. At higher temperatures, this ordered network is broken to release cations and anions from the network and form ion pairs. As this process involves an increase in the total entropy of the solution, it is called "entropy-driven association" [80,81].

### 4.4. Frequency dependence of the conductivity

The ionic conductivity discussed above was evaluated from the impedance spectra with the low frequency limit as  $\sigma[0]$ . The observed conductivity  $\sigma[\omega]$  showed frequency dependence, as can be seen in Fig. 7, where the conductivity increased in the high-frequency region following the power law of  $\sim \omega^{0.65}$ . This is typical behavior of the Jonscher region [82,83]. From the fitting of Eq. (6) to the experimental results, we evaluated the conductivity relaxation time  $\tau_{\alpha}$ , which is shown in Fig. 8 as a function of the inverse temperature.

Theoretical background of the frequency dependence of ionic conductivities has been discussed over recent decades by several researchers; for example, the coupling model [84], MIGRATION (MIsmatch Generated Relaxation for the Accommodation and Transport of IONs) concept [65], random barrier model [83], etc. in the field of solid ion conductors. On the other hand, in the field of glass-forming liquids or supercooled liquids, it is often related to the  $\alpha$  and  $\beta$  relaxation or mode-coupling  $\beta$ -process [10,40,41]. It has been also discussed in relation to the anomalous diffusion or sub-diffusion in restricted space, where the mean square displacement  $\langle x^2 \rangle$  of an ion is not proportional to time but instead obeys  $\langle x^2 \rangle t^n$ , (n < 1), which gives  $\sigma[\omega] \sim \omega^{1-n}$  [85,86]. A fractional derivative of Fokker-Planck [86,87] or generalized Langevin equations [86,88–90] have been applied to describe anomalous diffusion.

To analyze the short time-scale dynamics of ions in the liquid and supercooled liquid state, it is convenient to employ the well-established memory function formalism using the generalized Langevin equations [7,70,91–93],

$$m\frac{dv}{dt} + m\int_{0}^{t}\gamma(t-t')v(t')dt' = f(t),$$
(10)

where *m* and *v* are the mass and velocity, respectively, and  $\gamma(t)$  and f(t) are the memory function and fluctuating forces, respectively. From this formalism, the frequency-dependent diffusion coefficient is evaluated using the velocity-velocity self-correlation function as follows:  $D[i\omega] = \int_0^\infty \langle v(0)v(t) \rangle e^{-i\omega t} dt$  and is written as

$$D[i\omega] = v_0^2 \frac{1}{i\omega + \hat{\gamma}[i\omega]},\tag{11}$$

where *d* is the dimension and  $\hat{\gamma}[i\omega]$  is the Fourier-Laplace transform of the memory function  $\gamma(t)$ . From Eq. (11) with the equipartition theorem $v_0^2 = k_B T/m$ , the diffusion coefficient is given as follows:

$$D[0] = \frac{k_B T}{m \hat{\gamma}[0]}.$$
(12)

Conductivity is described from the current correlation. The general form of conductivity consists of the velocity correlation of the auto term and the cross term. If we assume cross velocity correlations to be zero, the DC conductivity is given by the Nernst-Einstein law (9) as follows:

$$\sigma[0] = \frac{nq^2}{m\hat{\gamma}[0]}.$$
(13)

The term  $\hat{\gamma}[0]$  is independent of the form of the memory kernel  $\gamma(t)$  but determined only from the time integration of  $\gamma(t)$ , which is estimated as  $\gamma(0) = 7.2 \times 10^{21} \text{ s}^{-1}$  at 143.4 K from the experimental result of DC conductivity, where mass *m* of the charge carrier lithium is  $1.15 \times 10^{-26}$  kg. Then, the frequency-dependent diffusion coefficient (Eq. (11)), and the conductivity are inversely proportional to  $\hat{\gamma}[i\omega]$  in the low-frequency region,  $i\omega \ll \hat{\gamma}[i\omega]$ . If we employ a Cole-Cole type form for the memory kernel,

$$\hat{\gamma}\left[i\omega\right] = \frac{\hat{\gamma}\left[0\right]}{\left[1 + (i\omega\tau_{\sigma})^{n}\right]},\tag{14}$$

the frequency-dependent conductivity is reduced to Eq. (6) in the lowfrequency region. The time constant  $\tau_{\sigma}$  corresponds to the specific time of the ions moving within a restricted area after which the ions can be regarded as if they have diffused in a quasi-homogeneous matrix with a macroscopic diffusion coefficient of D[0]. The relation between the memory kernel and fluctuational force is known as the second fluctuation-dispersion theorem,  $\langle f(0)f(t) \rangle = mk_B T\gamma(t)$ , where friction is calculated from the time integration of the fluctuational force correlation. Friction of  $m \int \gamma(t) dt = 6\pi\eta r$  corresponds to the Stokes law [94,95].

The time dependence of the correlation function is interesting and has been studied previously [96,97]. If the fluctuational force correlation shows a simple exponential decay, *n* is close to 1 in Eq. (14). We can immediately conclude that correlation function is not a simple exponential decay from the experimental result of frequency with conductivity, which could be analyzed using Eq. (6) with n = 0.65. A well-known expression for a complex exponential function is the stretched exponential function, i.e.  $\exp[-(t/\tau)^{\beta}]$  [82]. The other expanded form of exponential function is the Mittag-Leffler function, which is applied to study anomalous diffusion [86,87]. The Cole-Cole function of electric permeability is defined by the Mittag-Leffler function of Eq. (15):

$$\gamma(t) = \frac{\hat{\gamma}[0]}{\tau_{\sigma}} t^{n-1} E_{n,n} \left[ -\left(\frac{t}{\tau_{\sigma}}\right)^n \right],$$
(15)

where E corresponds to the Mittag-Leffler function

$$E_{\alpha,\beta}(x) = \sum_{n=0}^{\infty} \frac{x^n}{\Gamma(\alpha n + \beta)}$$
(16)

Therefore, we concluded that the origin of the Joncher-type frequency dependence of conductivity was the fluctuational force correlation described in Eq. (15). It is unclear why ions in a glassy solid or viscous liquid commonly show fluctuational force correlation, as shown in Eq. (15); however, this may be resolved by investigating the interactions or structures around the mobile ions.

#### 4.5. NMR correlation time from $T_1$ data

#### 4.5.1. <sup>1</sup>H nucleus

 $T_1$  relaxation times of the proton and lithium nuclei in lithium halide solutions have been reported extensively [28,29,36,47,48,61,62]. The relaxation mechanism of <sup>1</sup>H is dipole–dipole interaction. The  $T_1$  relaxation of protons has been separated into two categories: intra- and intermolecular interactions [28,29,62]. The intramolecular interaction is the dipole–dipole interaction between two protons in a water molecule, where the relaxation is induced by the rotational motion of the water molecule. The  $T_1$  relaxation time corresponding to the rotational motion is expressed as follows [28,99]:

$$\left(\frac{1}{T_{\rm l}}\right)_{1H} = \frac{3}{10} \left(\frac{\mu_0}{4\pi}\right)^2 \frac{\gamma_H^2 \hbar^2}{r^6} \left(\frac{\tau_H}{1 + (\omega_H \tau_H)^2} + \frac{4\tau_H}{1 + 4(\omega_H \tau_H)^2}\right). \tag{17}$$

Here,  $\tau_H$  is the correlation time of the rotational motion of water molecules,  $\mu_0$  and  $\gamma_H$  are the magnetic permeability of the vacuum and

gyromagnetic ratio of the proton, respectively, and *r* is the distance between the two protons. The contribution of the intermolecular interaction was found to be dominant at high temperatures [28,29]. It was approximately half of the total relaxation rate at 298 K and smaller in magnitude in the low-temperature region near the glass transition temperature [28]. The dipole coupling constant  $\frac{\mu_0}{8\pi^2} \frac{r_i}{r^3}$  was estimated from the maximum value of the relaxation rate, which is 23.0 kHz from this experiment. The theoretical value is 36.3 kHz using r = 1.49 Å from neutron scattering data for LiCl·6H<sub>2</sub>O [13]. The smaller value of the observed coupling constant than the calculated one was likely due to the geometry of water and the coordinated structure [62].

# 4.5.2. <sup>7</sup>Li nucleus

As the <sup>7</sup>Li nucleus has spin I = 3/2 and a quadrupole moment, several possible relaxation mechanisms have been discussed for aqueous lithium salt solutions [48,61,100]. The possible relaxation mechanisms are quadrupole interaction and dipole–dipole interaction. Although small amounts of dipole–dipole interaction [48,100] exist, this is reported to be negligible in a concentrated LiCl salt solution [61]. Quadrupole interaction of the first dominant term is between the quadrupole moment of spin I = 3/2 <sup>7</sup>Li and the fluctuation of the electric field gradient at the nucleus [28]. The fluctuations in the electric field gradient are induced by the motion of the lithium ion and/ or solvating water molecules, which affects  $T_1$  relaxation as follows:

$$\left(\frac{1}{T_{\rm l}}\right)_{7Li} = \frac{2}{25}\pi^2 \left(\frac{eQq}{h}\right)^2 \left(\frac{\tau_{Li}}{1+(\omega_{Li}\tau_{Li})^2} + \frac{4\tau_{Li}}{1+4(\omega_{Li}\tau_{Li})^2}\right),\tag{18}$$

where eQ and q are the quadruple moments of the <sup>7</sup>Li nucleus and the electric field gradient at the <sup>7</sup>Li nucleus, respectively. The quadrupole coupling constant(eQq/h) can be estimated from the maximum value of the relaxation rate (38.0 kHz). The quadrupole coupling constant of the LiI·9.25H<sub>2</sub>O solution was reported to be 38.4 kHz and had negligible concentration dependence [48]. It has been reported to be 43.1 kHz [28] for LiCl<sup>-7</sup>H<sub>2</sub>O solution and 41.2 kHz [36] for LiBr<sup>-7</sup>H<sub>2</sub>O; thus, the influence of the anion was less than 10%. The value of the electric field gradient q was calculated from the quadruple coupling constant to be  $3.93 \times 10^{19}$  V/m<sup>2</sup>. This value is in good agreement with the value of  $3.99 \times 10^{19} \, \text{V/m}^2$  calculated using Gaussian09 for [Li(H\_2O)\_4] ^+, where the Hartree-Fock method with 6-31G basis function was utilized. This meant that the contribution of the electric field gradient for the lithium nucleus was primarily from the water molecules in the first coordination shell. From the  $T_1$  values of <sup>1</sup>H and <sup>7</sup>Li, the correlation times  $\tau_{\rm H}$  and  $\tau_{\rm Li}$  were calculated using Eqs. (17) and (18), which are plotted in Fig. 8 by blue and red squares.

## 4.6. Comparison of different correlation times

In the previous sections, we derived various correlation times as  $\tau_{\sigma}$  from AC conductivity,  $\tau_{\rm H}$ , and  $\tau_{\rm Li}$  from  $T_1$  relaxation times of <sup>1</sup>H and <sup>7</sup>Li NMR. These were compared with the  $\tau_{\sigma \rm dc}$  values from the DC conductivity measurements, as described below (Fig. 8).

# 4.6.1. Conductivity relaxation time

It is well known that the characteristic time  $\tau_{\sigma}$  in Eqs. (6) and (14) derived from the frequency-dependent conductivity is inversely proportional to the DC conductivity,  $1/\tau \propto \sigma_0$  [82]. In fact, a good relation of  $\tau_{\sigma} = 1.50 \times 10^{-12}/\sigma_0$  s was observed in the present results. Therefore, we estimated  $\tau_{\sigma dc}$  from the DC conductivity, as plotted in Fig. 8. The solid line corresponded to VTF analysis as follows:

$$\tau = \tau_0 \exp\left(\frac{B}{T - T_0}\right) \tag{19}$$

These parameters are the same as those obbbtained using VTF for the temperature dependence of DC conductivity, i.e., B = 432 K,  $T_0 = 133$  K, and  $\tau_0 = 1.50 \times 10^{-12}/\sigma_0 = 1.15 \times 10^{-12}$  s.

# 4.6.2. NMR correlation times of ${}^{1}H$ and ${}^{7}Li$

The correlation time of <sup>1</sup>H ( $\tau_{\rm H}$ ) was in good agreement with that of <sup>7</sup>Li ( $\tau_{\rm Li}$ ) in the low-temperature region, as shown in Fig. 8. This suggested that the rotational Brownian motion of the water molecules coordinated to the lithium ions induced fluctuations in the electric field gradient at the <sup>7</sup>Li nucleus, which is in accordance with the previous work on LiI·6H<sub>2</sub>O [48]. However, the <sup>1</sup>H correlation time was found to be smaller than that of <sup>7</sup>Li in the high-temperature region (blue squares and red circles in Fig. 8). This is probably due to the intermolecular dipole interactions of the two protons in different water molecules, i.e., <sup>1</sup>H relaxation. As described before, the contribution of the intermolecular interactions is small at low temperatures, but it is approximately half of the total relaxation rate at 298 K [28]. The ratio of the two correlation times,  $\tau_{1\rm H}/\tau_{7\rm Li}$  is 0.55 at 290 K in the present study. This value is in good agreement with the contribution from intermolecular interactions.

## 4.6.3. Conductivity correlation time and NMR correlation times.

The correlation time calculated from the  $T_1$  of <sup>7</sup>Li NMR ( $\tau_{\text{NMR 7Li}}$  in Fig. 8) was in good agreement with that of DC conductivity ( $\tau_{\sigma\text{DC}}$ ) at high temperature, which meant that conductivity was mainly determined by the translational motion of the lithium ions. However, it deviated in the low-temperature region, whereby  $\tau_{\sigma}$  increased rapidly following the VTF law, although  $\tau_{\text{NMR 7Li}}$  and  $\tau_{\text{NMR 1H}}$  seemingly remained small and followed the Arrhenius law. Similar behavior has been reported previously for LiCl solutions [29,35,42]. This deviation is explained by considering the decoupling of a local  $\beta$ -mode from the macroscopic  $\alpha$ -mode at low temperature, which is related to the so-called Johari-Goldstein type  $\beta$ -relaxation branch [41]. The NMR  $T_1$  is coupled with the  $\beta$ -process at low temperature, although  $\tau_{\sigma}$  is coupled with the NMR  $T_1$  relaxation.

In this case, the total NMR correlation time  $\tau_{\rm NMR}$  is expressed as

$$\tau_{NMR}^{-1} = \tau_{\alpha}^{-1} + \tau_{\beta}^{-1},\tag{20}$$

where  $\tau_{\alpha}$  is the correlation time of the  $\alpha$ -relaxation following the VTF form (Eq. (19), solid curve in Fig. 8) and  $\tau_{\beta}$  is the correlation time for the  $\beta$ -process, which obeys the Arrhenius-type relation as follows:

$$\tau = \tau_0 \exp\left(\frac{E}{k_B T}\right) \tag{21}$$

The curve fitting of Eq. (20) to the observed  $\tau_{\rm NMR \ 7Li}$ , as shown by the dotted curve in Fig. 8, gives  $\tau_0 = 6.63 \times 10^{-13}$  s and E = 0.136 eV. The origin of the  $\beta$ -process in the LiI-6H<sub>2</sub>O solution is not yet clear; although it can probably be explained by the fast local orientational fluctuation of the remaining water molecules, whose macroscopic translation ( $\alpha$ -process) is slowed down and frozen below  $T_g$  [29]. The  $\tau_{\rm NMR \ Li}$  is determined by the fluctuation of the electric field gradient q at the <sup>7</sup>Li nucleus, which is made by the dipole moments of the surrounding water molecules. Thus, both the translational motion of the water molecules and their local orientational fluctuation affected the  $T_1$ values of <sup>7</sup>Li NMR. Similar considerations are also applicable to  $\tau_{\rm NMR \ 1H}$ , which is in good agreement with those of  $\tau_{\rm NMR \ 7Li}$  at low temperatures, as they are both determined by the orientational fluctuation of water molecules hydrating the lithium ions, which corresponds to the  $\beta$ -process in this liquid.

#### 5. Conclusion

To determine the effect of the anion size on the ion transport dynamics in a typical "coupled system" of LiX·RH<sub>2</sub>O, DSC, AC impedance, and PGSE-NMR analyses were performed.

From the DSC measurements of the Lil- $RH_2O$  systems (R = 4-10), the most stable glass-forming composition was found to be one with R = 6, where the glass transition temperature  $T_g$  was 143 K. The

conductivity and diffusion measurements of LiI-6H<sub>2</sub>O revealed that the temperature dependence of these parameters followed the VTF law, similar to the LiCl·*R*H<sub>2</sub>O system; however, the lithium diffusion coefficient and conductivity of LiI-6H<sub>2</sub>O were approximately twice as large than that of LiCl·7H<sub>2</sub>O at ~180 K and estimated to be several orders larger at  $T_{g}$ . This could be explained by the larger size of the iodide anion than that of the chloride anion. A small difference was found between the conductivity and diffusion coefficient at high temperatures, which violated the Nernst-Einstein law and could be attributed to cation–anion pairing or cross-correlation effects.

To assess the short time-scale dynamics of the supercooled liquid state, the frequency dependence of conductivity was analyzed. The conductivity relaxation time ( $\tau_{\sigma}$ ) and  $T_1$  relaxation times of <sup>7</sup>Li and <sup>1</sup>H nuclei were measured, from which the NMR correlation times ( $\tau_{\text{NMR}}$ ) were estimated. The  $\tau_{\sigma}$  followed the same VTF law of  $\alpha$ -relaxation as DC conductivity, which was due to the strong coupling of lithium ions to the surrounding water networks and suppression of the macroscopic transport of the lithium ions.

On the other hand, the NMR correlation times ( $\tau_{\rm NMR}$ ) deviated from the VTF law to Arrhenius-type at low temperatures, similar to the previous reports on LiCl·RH<sub>2</sub>O. This deviation was attributed to the fast Johari-Goldstein  $\beta$ -relaxation, which originated from the remaining fast local restricted rotation or orientational fluctuation of the water molecules.

#### CRediT authorship contribution statement

**Reiji Takekawa:** Conceptualization, Investigation, Writing - original draft. **Junichi Kawamura:** Conceptualization, Writing - review & editing, Supervision.

## **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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