^{7}Li-NMR Studies on Molecular Motion of Hydrated Lithium Ions in Concentrated Aqueous Solutions of LiCl, LiBr, and LiSCN at Low Temperatures

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Dedicated to Prof. Hitoshi Ohtaki on the occasion of his 60th birthday

Nuclear spin-lattice relaxation times, T_1, of ^{7}Li in 13.8 mol/kg $LiCl-H_2O$ and 12.3 mol/kg $LiCl-D_2O$ solutions have been measured in the temperature range 80 K–313 K. They showed similar temperature dependences with the same minimum values (27 ± 1 ms) which proved that the electric quadrupole interaction is dominant for the relaxation of ^{7}Li-NMR. The T_1 and T_2 values of ^{7}Li-NMR in concentrated aqueous solutions of LiCl (8–14 mol/kg), LiBr (8–10 mol/kg) and LiSCN (8–14 mol/kg) at 80 K to 300 K have been studied to obtain information concerning the dynamic properties of Li^+ ions and the effect of anions. T_1 at temperatures higher than the glass transition point is governed by a tumbling motion of the hydrated lithium ions.

Introduction

The properties of aqueous lithium chloride solutions have intensively been studied by differential thermal analyses (DTA) [1–3], X-ray diffraction [4], neutron scattering [5–7] and nuclear magnetic resonance (NMR) [8–15]. In particular the microscopic structure of $LiCl \cdot 5H_2O$ at low temperatures has recently been studied and the temperature dependent structure of hydrated Li^+ and Cl^- was found [4].

Recently we found by DTA that aqueous solutions of LiCl and LiSCN in the concentration range 8–14 mol/kg, and LiBr in the range 8–10 mol/kg remain liquid for at least 50 hours at temperatures slightly above their glass transition points [3]. This was not observed for aqueous $LiNO_3$ solutions up to 12 mol/kg, the solubility limit.

Useful information about molecular motions can be obtained from NMR relaxation data provided the relaxation mechanism is known. This is, however, not the case for ^{7}Li-NMR in aqueous LiCl solutions. In the present work we have therefore studied in detail the relaxation mechanism of ^{7}Li-NMR in 13.8 mol/kg $LiCl-H_2O$, and 12.3 mol/kg $LiCl-D_2O$ at low temperatures. Also measurements of T_1 and T_2 of ^{1}H- and ^{7}Li-NMR in aqueous solutions of LiCl, LiBr and LiSCN have been performed at 80–300 K.

Experimental

Reagent grade anhydrous LiCl (Wako Pure Chemicals), $LiBr \cdot H_2O$ (Kanto Chemicals) and LiSCN $\cdot 2H_2O$ (Kanto Chemicals) were used without further purification. A 12.3 mol/kg $LiCl-D_2O$ solution was prepared by dissolving anhydrous LiCl in D_2O (99.75% Junsei Pure Chemicals). The other solutions were prepared from deionized water, the resistivity of which was higher than 100 MΩ cm^{-1}. The concentrations of lithium ions in the samples were determined gravimetrically. The solutions were filtered through a glass filter (type G4) and filled into glass ampoules of 10 mm outside diameter. The specimens were degassed by freeze-pump-thawing before sealing.

^{7}Li-NMR line shapes were measured in the $LiCl-D_2O$ solution at room temperature (using a Bruker AC200P NMR machine operating at 78 MHz, and in the glassy 13.8 mol/kg $LiCl-H_2O$ solution at 129 K, using a Bruker CXP pulsed NMR spectrometer operating at 10 MHz. Measurements of ^{1}H- and ^{7}Li-NMR relaxation times were performed at 10 MHz using a

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Bruker pulsed NMR (CXP 4–60 MHz) spectrometer. The spin-lattice relaxation time T_1 was measured by using both the recovery method ($\pi/2-\tau-\pi/2$ pulse sequence) and the saturation recovery method $\{(\pi/2-t)_5-\pi/2-\tau-\pi/2$ pulse sequence with the condition $T_2^* < t \ll T_1$, T_2^* being a time constant for the NMR free induction decay in the presence of magnetic field inhomogeneity$\}$. The spin-spin relaxation time (T_2) was measured by the Carr-Purcell-Meiboom-Gill method [16, 17] for $T_2 \geqq T_2^*$. For $T_2 < T_2^*$, T_2 was obtained by correcting T_2^* for the inhomogeneity effects of the magnet. The T_1 and T_2 measurements were carried out between roughly 80 K and 300 K. The temperature was measured with a chromel-P/constantan thermocouple with an accuracy of ±0.3 K, and was controlled to within 0.1 K.

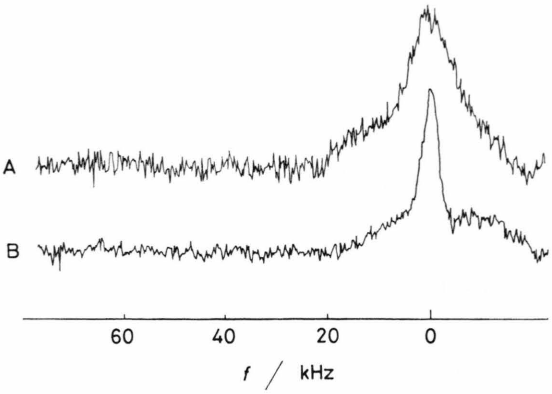

Fig. 2. ^{7}Li-NMR line shapes for the glassy state (at 129 K) of 13.8 mol/kg $LiCl-H_2O$ (A) and 12.3 mol/kg $LiCl-D_2O$ (B).

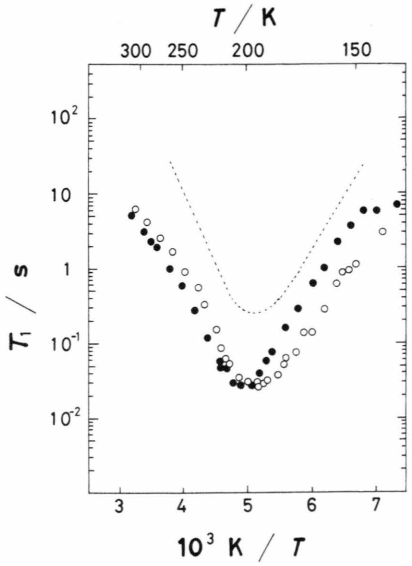

Fig. 3. Temperature dependence of ^{7}Li-NMR spin-lattice relaxation times at 10 MHz. ●: 12.3 mol/kg $LiCl-D_2O$; ○: 13.8 mol/kg $LiCl-H_2O$. The dotted line shows the calculated value of T_1 for the $LiCl-D_2O$ sample being responsible for dipolar relaxation.

Results

^{7}Li-NMR absorption lines for 12.3 mol/kg $LiCl-D_2O$ solution are shown in Figs. 1 and 2 for the liquid and the glassy state (together with the line for the 13.8 mol/kg $LiCl-H_2O$ solution), respectively. Splittings for the liquid sample were not observed. The line shapes for the glassy state were typical for a first-order quadrupole interaction of a spin 3/2.

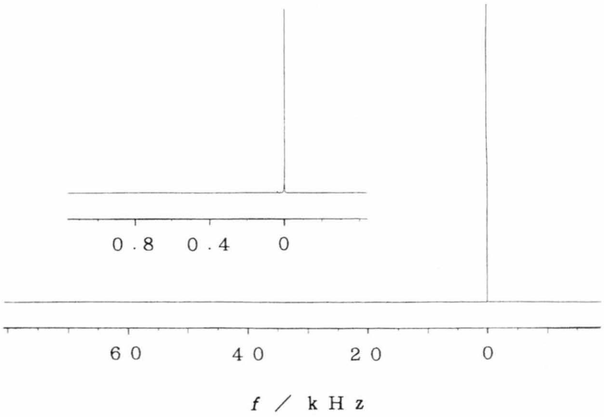

Fig. 1. High resolution ^{7}Li-NMR spectrum of 12.3 mol/kg $LiCl-D_2O$.

The recovery of magnetization over one decade exhibited a single exponential behaviour over the whole temperature range of the measurements. T_1 of the ^{7}Li-NMR is plotted against $1/T$ in Fig. 3 for the 12.3 mol/kg $LiCl-D_2O$ and the 13.8 mol/kg $LiCl-H_2O$ solutions. The T_1 minimum occured at 27±1 ms. The temperature was 202.0 K for the $LiCl-D_2O$ solution and 194.0 K for the $LiCl-H_2O$ solution. The temperature shift of the T_1 minimum is clearly outside of our experimental error. This shift may be a consequence of the dynamic isotopic effect on the molecular mobility.

Figure 4 where T_1 and T_2 are plotted against the inverse temperature, is a typical example of the ^{1}H- and ^{7}Li-NMR relaxation times from the 8 mol/kg solution of LiBr. Minima in the temperature depen-

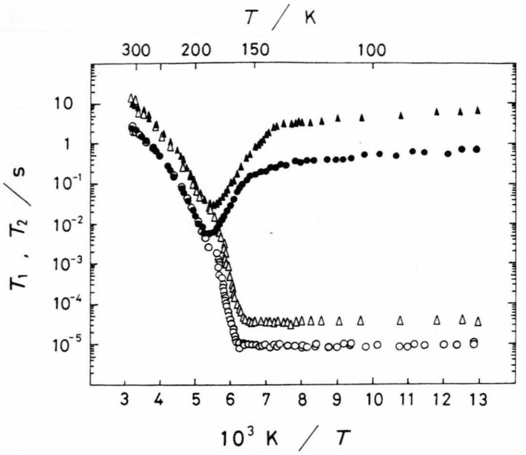

Fig. 4. Temperature dependence of ^{1}H- and ^{7}Li-NMR relaxation times at 10 MHz on 8 mol/kg LiBr. T_1 (●) and T_2 (○) for ^{1}H-NMR; T_1 (▲) and T_2 (△) for ^{7}Li-NMR.

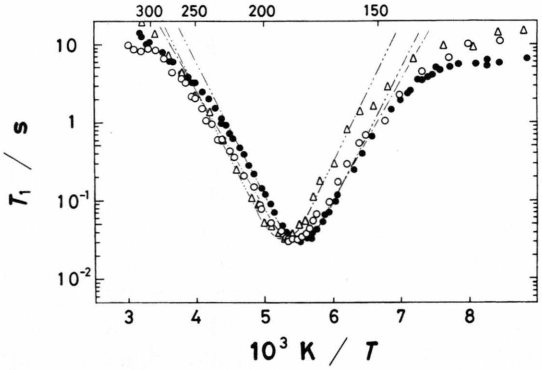

Fig. 5. Temperature dependence of ^{7}Li-NMR spin-lattice relaxation times at 10 MHz. ○: 8 mol/kg LiCl; ●: 8 mol/kg LiBr; △: 8 mol/kg LiSCN. Lines are the calculated values. –·–: 8 mol/kg LiCl; –··–: 8 mol/kg LiBr; –···–: 8 mol/kg LiSCN.

dence of T_1 where observed for both nuclei. Motional narrowing in T_2 with increasing temperature was observed. Similar temperature dependences of T_1 of ^{7}Li-NMR were observed for the 8 mol/kg solutions of LiCl, LiBr and LiSCN, as shown in Fig. 5, with slightly different temperatures of the T_1 minimum. The minimum values of T_1 and their temperatures obtained at various concentrations of LiCl, LiBr and LiSCN are tabulated in Table 1. With increasing concentration of LiCl the T_1 minimum decreases while the temperature of the T_1 minimum increases. This is more significant for the ^{1}H-NMR data.

Table 2 represents a comparison of the temperatures of the onset of the motional narrowing in T_2 with the glass transition temperature (T_g) determined by DTA. The temperatures of motional narrowing are 10–20 K higher than the glass transition temperatures. The gap in these temperatures is closely related to the difference in the time scale of the measuring techniques between DTA and NMR, and it could be one of the characteristics of the glass transition.

Analysis and Discussion

We have to consider two possible relaxation mechanisms of ^{7}Li-NMR because of the nuclear spin 3/2 of ^{7}Li: one is dipolar relaxation (dipole–dipole interaction between nuclei of ^{7}Li and ^{1}H) and the other is quadrupolar relaxation (NQR). NQR is usually considered to be the main cause of the relaxation in case nuclear spins $I > 1/2$. However, there exists a possibility of the dipolar relaxation since the hydrated lithium ion has a highly symmetric structure.

The nuclear dipole interaction of ^{7}Li and ^{1}H depends on the distance between the H nuclei, the nu-

Table 1. Minimum values of spin-lattice relaxation times of ^{7}Li- and ^{1}H-NMR at 10 MHz on aqueous solutions of LiCl, LiBr and LiSCN.

	^{7}Li-NMR						^{1}H-NMR					
(LiX)	LiCl		LiBr		LiSCN		LiCl		LiBr		LiSCN	
mol/kg	$T_{1\,min}$/ms	T/K	$T_{1\,min}$/ms	T/K	$T_{1\,min}$/ms	T/K	$T_{1\,min}$/ms	T/K	$T_{1\,min}$/ms	T/K	$T_{1\,min}$/ms	T/K
8	32 ± 1	184.5 ± 0.5	30 ± 1	181.5 ± 0.5	32 ± 2	188.7 ± 0.5	4.1 ± 0.1	187.3 ± 0.5	4.4 ± 0.1	183.5 ± 0.5	5.3 ± 0.3	192.3 ± 0.5
10	31 ± 1	186.9 ± 0.5	28 ± 1	181.8 ± 0.5	31 ± 1	193.1 ± 0.5	4.4 ± 0.2	189.8 ± 0.5	4.4 ± 0.1	184.2 ± 0.5	5.3 ± 0.3	196.1 ± 0.5
12	31 ± 1	190.5 ± 0.5			31 ± 2	198.4 ± 0.5	4.9 ± 0.3	192.7 ± 0.5			6.2 ± 0.2	199.2 ± 0.5
13.8	27 ± 1	194.0 ± 0.5					4.8 ± 0.1	195.0 ± 0.5				
14	26 ± 1	194.2 ± 0.5			31 ± 1	200.0 ± 0.5	4.9 ± 0.1	196.9 ± 0.5			6.2 ± 0.3	200.0 ± 0.5
12.3 (in D_2O)	27 ± 1	202.0 ± 0.5										

Table 2. Onset of motional narrowing of T_2 and glass transition temperatures (T_g) of aqueous solutions of LiCl, LiBr and LiSCN.

	T/K								
(LiX)	LiCl			LiBr			LiSCN		
mol/kg	^{1}H-NMR	^{7}Li-NMR	T_g	^{1}H-NMR	^{7}Li-NMR	T_g	^{1}H-NMR	^{7}Li-NMR	T_g
8			137.8 ± 1.2	158 ± 3	150 ± 5	136.2 ± 1.7	167 ± 1	163 ± 3	147.4 ± 0.3
10				160 ± 3	152 ± 2	139.2 ± 0.6	166 ± 4	164 ± 3	150.7 ± 0.3
12		155 ± 4	144.5 ± 0.3				171 ± 4	166 ± 3	154.3 ± 0.3
13.8		157 ± 1	147.8 ± 0.3						
14	161 ± 5	164 ± 5	148.7 ± 0.3				169 ± 6	167 ± 5	157.6 ± 0.3
12.3 (in D_2O)		171 ± 3	156.3 ± 0.3						

clear spin number, the gyromagnetic ratio of the nuclei and so on. In case of a hydrated lithium ion, the nuclear dipole interaction is mainly attributable to the ^{7}Li–^{1}H pair and is strongly affected by the water molecules attached to ^{7}Li. The interaction fluctuates by molecular tumbling and translational motion.

The quadrupole moment is fixed in the nucleus and oriented in a space-fixed direction by the interaction of the external magnetic field with the nuclear magnetic dipole moment. The electric-field gradient (EFG) at the nucleus is due to the electrons in the bond and fluctuates in orientation in the space-fixed axis system due to the molecular tumbling. Translational motion does not affect the orientation or magnitude of the EFG at the nucleus.

In the case of dipolar relaxation, the spin-lattice relaxation time $T_{1D-D}(\mathrm{Li-H})$, governed by molecular tumbling, is given using the BPP theory [18] and considering only intra-molecular contributions by

$$1/T_{1D-D}(\mathrm{Li-H}) = (\gamma_H^2 \gamma_{Li}^2 h^2)/(60\pi^2 r^6)\, n I_H (I_H+1) F(\omega_{Li}, \omega_H, \tau), \quad (1)$$

where

$$F(\omega_{Li}, \omega_H, \tau) = 2\tau/[1+(\omega_{Li}-\omega_H)^2\tau^2] + 6\tau/[1+\omega_{Li}^2\tau^2] + 12\tau/[1+(\omega_{Li}+\omega_H)^2\tau^2].$$

I_H is the nuclear spin number of ^{1}H, γ_H, and γ_{Li} are the gyromagnetic ratios of the nuclei ^{1}H and ^{7}Li, respectively, ω is the angular Larmor frequency for nucleus i, h is Planck's constant, r is the distance between ^{7}Li and ^{1}H, and n is the number of the pairs of ^{7}Li and ^{1}H in a hydrated Li$^+$ ion.

In the other case, the spin-lattice relaxation time, $T_{1Q}(\mathrm{Li})$, governed by the quadrupole interaction [19, 20], is given by

$$1/T_{1Q}(\mathrm{Li}) = (2\pi^2/25)(1+\eta^2/3)(e^2 Q q/h)^2 \cdot [\tau/(1+\omega_{Li}^2\tau^2) + 4\tau/(1+4\omega_{Li}^2\tau^2)], \quad (2)$$

where $(e^2 Q q/h)$ is the quadrupole coupling constant and η the asymmetry parameter.

If we substitute H_2O by D_2O, the expression of the spin-lattice relaxation time, $T_{1D-D}(\mathrm{Li-D})$, is given by

$$1/T_{1D-D}(\mathrm{Li-D}) = (\gamma_D^2 \gamma_{Li}^2 h^2)/(60\pi^2 r^6)\, n I_D (I_D+1) F(\omega_{Li}, \omega_D, \tau). \quad (3)$$

The ratio between $T_{1D-D}(\mathrm{Li-H})$ and $T_{1D-D}(\mathrm{Li-D})$ can be estimated using the gyromagnetic ratio of these nuclei and their nuclear spin numbers, i.e. $T_{1D-D}(\mathrm{Li-H})/T_{1D-D}(\mathrm{Li-D}) \sim [\gamma_D^2 I_D(I_D+1)/\gamma_H^2 I_H (I_H+1)] \sim 0.064$, assuming no change of geometrical factors in the molecules. The ratio of the minimum values of these relaxation times as a function of temperature is expected to be $T_{1D-D}(\mathrm{Li-D})_{\min}/T_{1D-D}(\mathrm{Li-H})_{\min} = 8.6$.

In the case of the quadrupolar relaxation, the spin-lattice relaxation time, $T_{1Q}(\mathrm{Li})$, given by (2) is strongly governed by intra-molecular contributions. Particularly it depends on the electric field gradient around the ^{7}Li nucleus. So the substitution of solvents will not make much difference in the spin-lattice relaxation rate. The T_1 data for sample of 13.8 mol/kg LiCl–H_2O and 12.3 mol/kg LiCl–D_2O give an important guide to assign the relaxation mechanism. The ratio of lithium ions to water molecules in these solutions is 1:4. The lithium ions are expected to be coordinated tetrahedrally with four water molecules and have an axial symmetric structure. It is plausible, therefore, to estimate the asymmetry parameter η in (2) to be zero because of the single line shape of the ^{7}Li-NMR absorption spectrum shown in Figure 1. The dotted line in Fig. 3 shows the calculated T_1 values for the LiCl–D_2O solution using (3) and (4), the molecular geometry obtained from the T_1 minimum, and the activation parameters ($E_a = 33.5$ kJ mol^{-1}, $\tau_0 = 1.2 \times 10^{-17}$ s) obtained by fitting (1) to the experimental T_1 data near the minimum for the sample of 13.8 mol/kg LiCl–H_2O. The experimental fact that the T_1 minima of ^{7}Li-NMR obtained in H_2O and D_2O are both at 27 ± 1 ms clearly demonstrates that the relaxation rate of ^{7}Li-NMR is governed by the quadrupolar interaction modulated by the molecular tumbling of hydrated lithium ions with the quadrupole coupling constant $(e^2 Q q/h) \sim 45.5$ kHz. The value $(e^2 Q q/h)/2$ of (~ 15 kHz), estimated from the line shape in Fig. 2, also supports our assumption indirectly. It may be reasonable to attribute a small quadrupole coupling constant to a symmetry quenching caused by the arrangement of water molecules around the Li^+ ion. Nevertheless its value is higher than the value expected from the outer sphere contribution. The value of $e^2 Q q/h$ obtained from the relaxation data for the liquid seems to be larger than the value obtained from the line shape for the glassy state. There is a remaining contribution from the first coordination sphere which indicates deviations from the cubic symmetry during the NMR observation time. The ^{7}Li nuclear quadrupole coupling constant was discussed in detail for the aqueous LiI solution in [21], so we do not mention it here.

Now, we can discuss the molecular motion of the lithium ions in the solutions based on the relaxation mechanism discussed above. In order to obtain the correlation time τ by fitting the T_1 data of Fig. 5 to (2), we assume the asymmetry parameter η to be zero, since the T_1 minima of ^{7}Li-NMR are much the same for all solutions examined. The correlation times thus obtained for 8 mol/kg solutions of LiCl, LiBr and LISCN are plotted against $1/T$ in Figure 6. Linear relationships are found in the temperature region (around the T_1 minimum) between 150 K and 250 K for these samples. The temperature dependence of the correlation times for other solutions examined were found to be similar to those shown in Figure 6. Activation parameters were obtained assuming the Arrhenius equation for the linear portion of the correlation time in Figure 6:

$$\tau = \tau_0 \exp(E_a/RT). \tag{4}$$

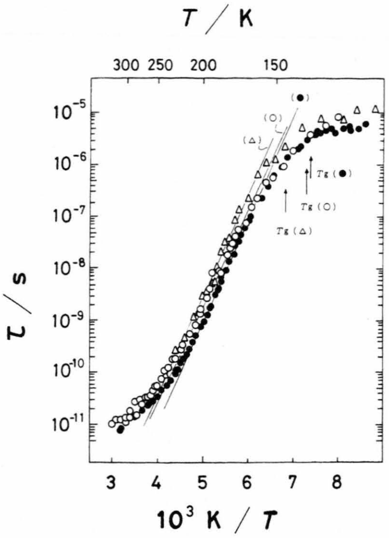

Fig. 6. Temperature dependence of the correlation times for molecular tumbling of hydrated lithium ions in aqueous solutions of lithium salts. ○: 8 mol/kg LiCl; ●: 8 mol/kg LiBr; △: 8 mol/kg LiSCN.

The activation parameters obtained for all examined solutions are listed in Table 3. The broken lines in Fig. 5 are the calculated T_1 values for 8 mol/kg samples of LiCl, LiBr and LiSCN using (2) and assuming η to be zero, the coupling constant obtained from the T_1 minimum value and these activation parameters. These lines fit well the experimental values except for the regions of higher and lower temperatures in Figure 5. The activation energies are independent of the concentration of the solutions but depend on the anions; the larger the anions, the greater become the activation energies. It is interesting to note that the activation energies obtained here are by about fifty percent larger than the hydrogen-bond energy in pure water, and also larger by a factor of two than the activation energies of tumbling of similar size globular organic molecules in the plastic crystal phase [22, 23]. This comparison indicates that the tumbling motion of the hydrated lithium ions in the low temperature solutions is affected not only by hydrogen-bonds but also other factors such as geometric effects of anions.

The relaxation of ^{1}H-NMR could be attributed mainly to the dipolar interaction between ^{1}H nuclei in water molecules. The motions of water molecules which contribute to the relaxation may be much more complicated than the molecular motion of lithium ions. A significant contribution from chemical ex-

Table 3. Activation parameters for molecular tumbling of hydrated lithium ions in aqueous solutions of LiCl, LiBr and LiSCN.

	LiCl		LiBr		LiSCN	
(LiX) / mol/kg	E_a / kJ/mol	$10^{17}\,\tau_0$ / s	E_a / kJ/mol	$10^{18}\,\tau_0$ / s	E_a / kJ/mol	$10^{18}\,\tau_0$ / s
8	29.5 ± 0.7	$3.9\pm^{2.2}_{1.4}$	33.4 ± 1.0	$2.3\pm^{1.9}_{1.1}$	34.2 ± 1.3	$3.7\pm^{3.87}_{1.9}$
10	29.5 ± 1.0	$4.9\pm^{3.6}_{2.1}$	33.9 ± 0.8	$2.0\pm^{1.2}_{0.8}$	35.5 ± 0.7	$2.4\pm^{1.2}_{0.8}$
12	29.9 ± 1.2	$6.7\pm^{8.1}_{3.6}$			33.8 ± 2.3	$14\pm^{42}_{10}$
13.8	29.1 ± 1.3	$12\pm^{14}_{6}$				
14	27.9 ± 0.8	$32\pm^{17}_{11}$			33.4 ± 1.4	$14\pm^{14}_{8}$
12.3 (in D_2O)	31.1 ± 1.0	$8.3\pm^{6.5}_{3.6}$				

change or translational motion of water molecules to the relaxation should be taken into account in addition to the contribution from the molecular tumbling of hydrated lithium ions. Therefore we do not discuss the ^{1}H-NMR data in this paper; a study along these lines is now in progress.

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