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Isotope Effects on the Reorientational Motion of Hydrated H_2O Molecules in Alkali Metal Bromide Dilute Aqueous Solutions Studied by NMR Spectroscopy

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(Received July 21, 1990)

The spin-lattice relaxation times of ^1H and ^{17}O nuclei of hydrated H_2O molecules in alkali metal bromide (LiBr, NaBr, KBr, and CsBr) dilute aqueous solutions in the concentration range from 0.2 to 1.0 mol kg^{-1} at 25 °C were measured by NMR spectroscopy. The reorientational correlation times for the intramolecular ^1H–^1H (τ^{+}_{HH}) and ^1H–^{17}O (τ^{+}_{OH}) axes, as well as the perpendicular axis (^{17}O nuclei, $\tau^{+}_{^{17}\mathrm{O}}$) to the molecular plane of a hydrated H_2O molecule were determied. The two reorientational correlation times (τ^{+}_{HH} and τ^{+}_{OH}) of pure H_2O and hydrated H_2O molecules in Li^+, Na^+, K^+, and Cs^+ ions were equal, respectively. Comparing previous data for hydrated D_2O molecules with that calculated by using correction values (r_{HH}, r_{OH}, and quadrupolar constant) for H_2O molecules, the ratios of $\tau^{+}_{\mathrm{D}}(D_2O)/\tau^{+}_{\mathrm{OH}}(H_2O)$ and $\tau^{+}_{^{17}\mathrm{O}}(D_2O)/\tau^{+}_{^{17}\mathrm{O}}(H_2O)$ were found to be of the same order as $\eta(D_2O)/\eta(H_2O)$, except for the $\tau^{+}_{^{17}\mathrm{O}}(D_2O)/\tau^{+}_{^{17}\mathrm{O}}(H_2O)$ value for the Li^+ ion.

To comprehend the complete picture regarding the dynamic properties of ionic hydration in water it is necessary to consider both macro- and microdynamic approaches. Regarding aqueous solutions, studies have accumulated many precise limiting values at infinite dilution regarding both the thermodynamic and transport properties.[1] On the other hand, our understanding concerning electrolyte solutions and the microdynamic properties of hydrated H_2O molecules of ions in water studied by NMR spectroscopy is very poor due to a lack of fundamental research concerning the concentration dependence, except for studies of Hertz et al.[2–5] and Leyte et al.[6–10] They have provided limiting values of the reorientational relaxation rates of hydrated water molecules of ions at infinite dilution by using a polynominal expression of the relaxation rates as a function of high concentrations, including both ion–ion and ion–water interactions.

Presently, the NMR technique that was developed is preferable for studying the reorientational motion of hydrated water molecules at lower concentrations, due to the ion–water interaction, to any other available experimental techniques. A study of the spin–lattice relaxation rates (R_1) of the ^1H, ^2D, and ^{17}O nuclei of water molecules in electrolyte solutions provides information about the reorientational motion of water molecules. The ^2D and ^{17}O relaxations are determined intramolecularly by quadrupole interactions, due to a rotational motion for the reorientation of the ^2D and ^{17}O electric field gradient tensor. The proton R_1 however, is governed by both intra and intermolecular ^1H–^1H dipolar interactions due to the reorientational and translational motions. The intra and intermolecular contributions to proton R_1 can be divided and determined from each theoretical expression by applying the extreme narrowing limit as well as measurements of the self-diffusion coefficient of water molecules by the spin–echo method;[2] it is also possible to study the ^1H relaxation in ^{17}O enriched water.[6]

From a previous study concerning the concentration dependence on the nuclear relaxation rates of the ^2D and ^{17}O nuclei of hydrated D_2O molecules of ions in dilute electrolyte solutions,[11] we found the both rates can be represented by linear functions against the concentrations of electrolyte solutions. The relationship between R_1 and the salt concentration is important for determining the limiting value, exclusively, due to the ion–water interaction on the base of the two-state model, i.e., hydrated water molecules and water molecules having a bulk water structure. By analysing these results, the reorientational motion along the O–D axis of the D_2O molecule was found to be 10% faster than those perpendicular to the D_2O molecular plane for the structure-making ions of Li^+ and Na^+ ions; for the structure-breaking ions of K^+ and Cs^+ ions, the tendency was inversed. This significant anisotropy regarding the reorientational motion of hydrated D_2O molecules in salt solutions comes from a local dynamic structure induced by a difference in the intermolecular interactions among ions, hydrated water molecules, and water molecules having a bulk water structure.

The local dynamic structure of hydrated water molecules in the vicinity of ions is strongly controlled by the solvent viscosity, which can be changed by various factors: i.e., temperature, pressure, solvent, and isotope effects. Though the isotope effect is a unique factor among them, no systematic study has been carried out by the NMR method. The dielectric properties of H_2O and D_2O are almost identical as most the other macroscopic properties.[12] The largest difference in the properties of pure water is its viscosity, which is 23% higher in D_2O than in H_2O at

25 °C.[13] Such differences as the thermodynamic properties of liquid H_2O and D_2O are consistent due to the O–D···O hydrogen bond being somewhat stronger than the O–H···O hydrogen bond. Therefore, in addition to the earlier study concerning the D_2O molecule,[11] NMR studies of the reorientational motion of H_2O molecules in dilute alkali metal bromide (LiBr, NaBr, KBr, CsBr) solutions have usefully helped to reach definite conclusions about both the hydration and anisotropy of the reorientational motion of hydrated water molecules of alkali metal ions in an H_2O system.

Experimental

Samples. Alkali metal bromide (LiBr, NaBr, KBr, CsBr) salts from Nakarai Tesque. Inc (extra-pure grade) were recrystallized from either water or ethanol. Deionized water was destilled with the addition of a small amount potassium permanganate. Sample preparation before an NMR measurement was reported previously.[11]

NMR Measurement. The ^1H relaxation times were measured on a JEOL GX-270 pulsed spectrometer operating at 270.0 MHz. Samples were kept in 4 mm diameter glass tubes and then inserted in 5 mm diameter glass tubes containing neat D_2O. The spin–lattice relaxation times (T_1) were measured by inversion-recovery methods, using a pulse sequence of 180°—t—90° pulses; The T_1 values were determined for each sample at 16 different time intervals (t), and the pulse delay time (PD) was more than $10T_1$. The frequency was 700 Hz for the ^1H nucleus. The free indicational decay of the ^1H nucleus was accumulated 4 times for all concentrations. Measurements of the ^{17}O nucleus relaxation times were carried out under the same condition which were reported previously.[11] The temperature was controlled to 25±0.1 °C by means of gas-thermostating.

Results and Discussion

Concentration Dependence of R_1 of H_2O Molecules in Aqueous Bromide Solutions. The relation between the spin–lattice relaxation rates ($R_1=1/T_1$) of the ^1H and ^{17}O nuclei of H_2O molecules and their concentrations in bromide solutions at 25 °C is shown in Figs. 1 and 2 and Table 1 along with data concerning the ^1H nucleus at 1 mol kg^{-1}, studied by Endom et al.[2] Our relaxation rates for the ^1H nucleus at 1 mol kg^{-1} agree with those of Endom et al.[2] within the experimental error. The ratios (R_1/R_1^0) vary linearly with increasing concentration up to 1.0 mol kg^{-1}. The R_1/R_1^0 (R_1^0 for pure H_2O) values are expressed as a linear function of the concentration, up to 1.0 mol kg^{-1}. Their values of ^1H and ^{17}O nuclei at a certain concentration are in the order LiBr>NaBr>KBr>CsBr. The structure-making salts of Li and Na increase the R_1/R_1^0 values of ^1H and ^{17}O of H_2O. On the other hand, the structure–breaking salts of K and Cs decrease the R_1/R_1^0 value of H_2O.

For ^1H and ^{17}O nuclei the concentration dependence of R_1 is given by linear equations at a concentration below 1.0 mol kg^{-1}, as follows:

$$R_1 = (1 + Bm)R_1^0, \tag{1}$$

where R_1 and R_1^0 are the spin–lattice relaxation rates at an electrolyte concentration of m and for pure H_2O, respectively. The B_H, $B_{^{17}O}$, and B_H–$B_{^{17}O}$ values are shown in Table 2 along with those of the D_2O system. From these results, the structure-making effect of Li and Na salts and the structure-breaking effect of K and Cs salts predominantly affect the B coefficient of the ^1H nucleus, rather than those of the ^{17}O nucleus of the

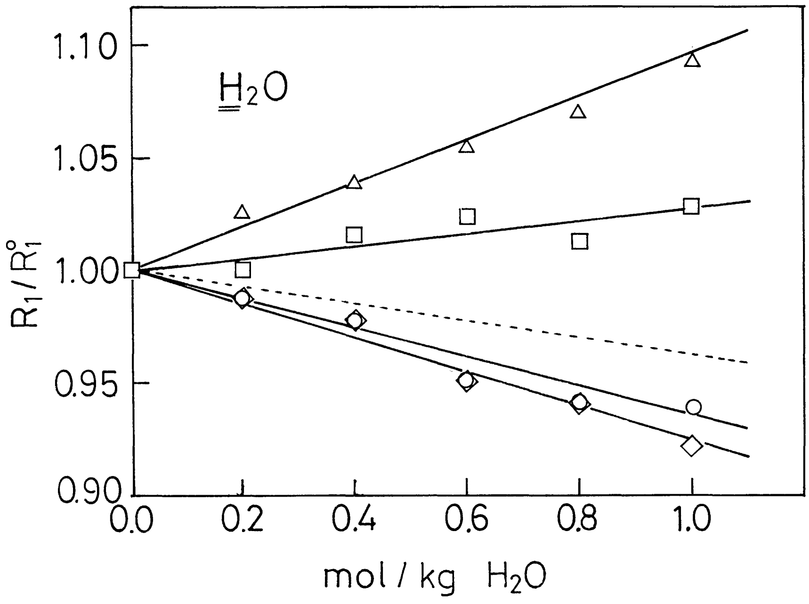

Fig. 1. Plots of H relxation rates (R_1/R_1^0) of a H_2O molecule in alkali metal bromide solutions at 25 °C. △: LiBr, □: NaBr, ○: KBr, ◇: CsBr, ---: KCl.

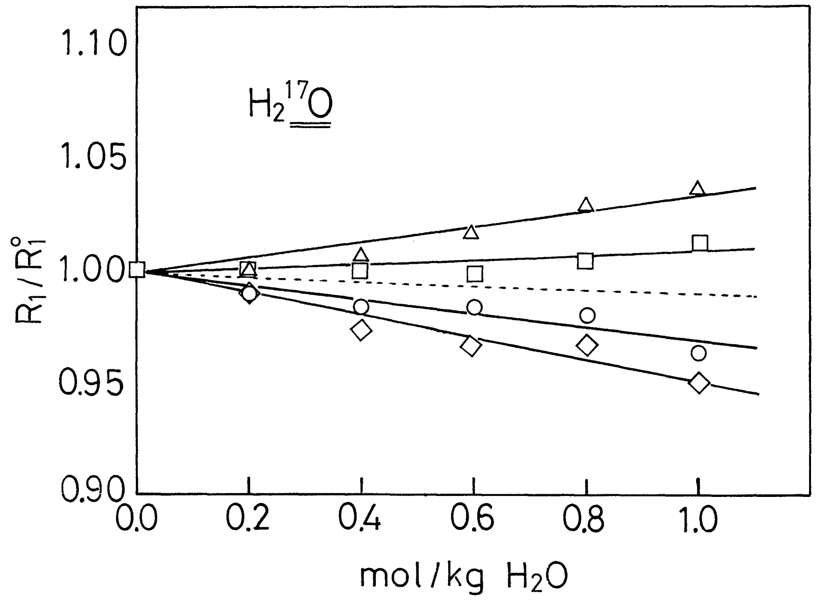

Fig. 2. Plots of ^{17}O relxation rates (R_1/R_1°) of a H_2O molecule in alkali metal bromide solutions at 25 °C. △: LiBr, □: NaBr, ○: KBr, ◇: CsBr, ---: KCl.

Table 1. The ^1H and ^{17}O Spin-Lattice Relaxation Rates R_1(s^{-1}) of a H_2O Molecule at 25 °C[a)]

Salt	H_2O/mol kg^{-1}									
	0.2		0.4		0.6		0.8		1.0	
	^1H	^{17}O	^1H	^{17}O	^1H	^{17}O	^1H	^{17}O	^1H	^{17}O
LiBr	0.289	138	0.292	139	0.297	140	0.301	142	0.307 (0.304)	143
NaBr	0.281	138	0.286	138	0.290	138	0.283	139	0.289 (0.290)	140
KBr	0.278	136	0.276	136	0.267	136	0.264	136	0.264 (0.265)	133
CsBr	0.278	137	0.277	134	0.269	133	0.265	134	0.259 (0.260)	131
KCl	0.278	138	0.274	137	0.273	137	0.277	137	0.273 (0.273)	137

a) For pure H_2O, the R_1 value of ^1H and ^{17}O are 0.281 and 138 s^{-1}, respectively. ( ) are data of Endom et al.[2)]

Table 2. The B_H, $B_{^{17}O}$, $B_H-B_{^{17}O}$, and B-Coefficient of Viscosity for Various Alkaline Metal Aqueous Solutions at 25 °C

Salt	B_H	$B_{^{17}O}$	$B_H-B_{^{17}O}$	B-coefficient[a)]
LiBr	0.096 (0.065)	0.031 (0.058)	0.065 (0.007)	0.108
NaBr	0.029 (0.010)	0.004 (0.010)	0.025 (0.000)	0.044
KBr	−0.066 (−0.060)	−0.034 (−0.032)	−0.032 (−0.028)	−0.049
CsBr	−0.073 (−0.074)	−0.053 (−0.047)	−0.020 (−0.027)	−0.087
KCl	−0.034	−0.011	−0.023	−0.014

a) Ref. 14. ( ) is D_2O systems in Ref. 11.

hydrated H_2O molecules of ions. There are no differences between the effect of the structure-breaking salts of K and Cs on the B coefficients of the both nuclei in H_2O and D_2O systems. However, the effect of the structure-making salts of Li and Na on the B coefficients of the ^1H nucleus in H_2O is enhanced more than those of the ^2D nucleus in D_2O; its effect on the B coefficient of the ^{17}O nucleus is vice versa to that in H_2O and D_2O systems. The correlation factors of the B coefficients between the NMR and viscosity of solutions are ca. 1.0 for B_H and ca. 0.4 for $B_{^{17}O}$.

Reorientational Motion of Hydrated H_2O Molecules. A linear relation between the relaxation rates and the salt concentration shown in Figs. 1 and 2 has been established in dilute salt solutions below 1.0 mol kg^{-1}. We can therefore consider that the ion–ion interaction is eliminated in this system and that each observed relaxation can be expressed as a weighted sum of the limiting relaxation rates in infinite dilution on the base of two state model, as follows:

$$(R_1)_X = (1 - x^+ - x^-)(R_1)_X^0 + x^+(R_1)_X^+ + x^-(R_1)_X^- \quad (2)$$

and

$$(R_1)_X/(R_1)_X^0 = 1 + x^+\{(R_1)_X^+/(R_1)_X^0 - 1\} + x^-\{(R_1)_X^-/(R_1)_X^0 - 1\}, \quad (3)$$

where $(R_1)_X^0$, $(R_1)_X^+$, $(R_1)_X^-$, x^+, and x^- are the spin–lattice relaxation rates of pure water, cation and anion hydrated water, and the mole fraction of the cation and anion, respectively. The subscript X can be ^{17}O, HH, or OH when the relaxation path is, respectively, ^{17}O quadrupolar, an intramolecular ^{1}H–^{1}H dipolar interaction, or an intramolecular ^{1}H–^{17}O dipolar interaction.

By defining a coordination number, $n^\pm$, the mole fraction $x^\pm$ can be expressed in terms of the molarlity m of the solution,

$$x^\pm = n^\pm \times m/55.5. \quad (4)$$

The observed proton, R_1, in H_2O molecules is given by intra and intermolecular ^{1}H–^{1}H interactions, as follows:

$$(R_1)_H = (R_1)_{HH}^{\text{intra}} + (R_1)_{HH}^{\text{inter}}. \quad (5)$$

As compared to $(R_1)_H$=0.281 s^{-1} at 25 °C, Hertz[13] obtained the $(R_1)_{HH}^{\text{inter}}$=0.106 s^{-1} using experimental data of the self-diffusion coefficients of water as well as the theoretical jumping model of translational motion. If we arbitrarily take this value, $(R_1)_{HH}^{\text{intra}}$ contributes 62% of $(R_1)_H$. Later, Lankhorst et al.[6] measured the ^{1}H relaxation rates in ^{17}O-enriched water as a function of the ^{17}O mole fraction, $\chi(^{17}O)$. In view of the observed lineality, they obtained

$$(R_1)_H = (R_1)_{HH} + \chi(^{17}O)R_{OH}. \quad (6)$$

Of course, the R_{OH} value is the sum of the intra- and intermolecular ^{1}H–^{17}O dipolar interactions. For various salt solutions and pure water, they observed that the average ratios, $(R_1)_H/(R_1)_{HH}$ and $(R_1)_H/(R_1)_{OH}$ (^{17}O is a natural abundance), for various salts are 1.00±0.02 and 1.03±0.10, respectively.[9,10] The intramolecular contribution to $(R_1)_{HH}$ is 57%, and the intermolecular contribution to $(R_1)_{OH}$ is 2%.[9,10] The ^{17}O nucleus relaxes intramolecularly by quadrupole interactions, and the observed relaxation rates are directly correlated to the intramolecular term. Assuming that $R_1^+(K^+)=R_1^-(Cl^-)$ is satisfied for a KCl solution, in the case of an equal splitting of the *B*-coefficient into an ionic component[11,14] in Eq. 3, the $(R_1)_{HH}^{+,\text{intra}}(R_1)_{OH}^{+,\text{intra}}$, $(R_1)_{^{17}O}^+$ values for various cations are determined from the both relations of the 57% intramolecular contribution to $(R_1)_{HH}$ and the 2% intermolecular contribution to $(R_1)_{OH}$. Table 3 shows the calculated R_1^+ values of ^{1}H and ^{17}O nuclei, and the $(R_1)_{HH}^{+,\text{intra}}$ and $(R_1)_{OH}^{+,\text{intra}}$ relaxation rates of intramolecular ^{1}H–^{1}H and ^{1}H–^{17}O dipolar interactions of hydrated H_2O molecules of the alkali metal ions. It was concluded that the intramoleculer contribution of ca. 62% to $(R_1)_{HH}^{+,\text{intra}}$ determined by Hertz et al.[15,16] is considerably overestimated.[10] Comparing the relaxation rates of the intramolecular ^{1}H–^{1}H dipolar interaction, the intramolecular ^{1}H–^{17}O dipolar interaction, and the ^{17}O quadrupolar interaction of hydrated H_2O molecules with those of pure H_2O molecules, the ^{1}H nucleus relative relaxation rate $((R_1)_{HH}^{+,\text{intra}}/(R_1)_{HH}^{0,\text{intra}}=(R_1)_{OH}^{+,\text{intra}}/(R_1)_{OH}^{0,\text{intra}}=(R_1)_H^+/(R_1)_H^0)$ are almost of the same order as the ^{17}O nucleus relative relaxation rates $((R_1)_{^{17}O}^+/(R_1)_{^{17}O}^0)$ for the structure-breaking ions of K$^+$ and Cs$^+$ ions. On the other hand, the structure-making effect of Li$^+$ and K$^+$ ions on the ^{1}H nucleus relaxation rates are larger than those of the ^{17}O nucleus.

Under extra narrowing conditions the intramolecular term of the spin-lattice relaxation rate, $(R_1)_X^{\pm,\text{intra}}$, of hydrated water molecules is the product of an interaction constant, $C_X^\pm$, and a reorientational correlation time, $\tau_X^\pm$:

$$(R_1)_X^{\pm,\text{intra}} = C_X^\pm \times \tau_X^\pm. \quad (7)$$

The intramolecular ^{1}H–^{1}H dipolar interaction is given by

$$(R_1)_{HH}^{\pm,\text{intra}} = \frac{3\gamma_H^4\hbar^2}{2r_{HH}^6}\tau_{HH}^\pm, \quad (8)$$

Table 3. The Relaxation Rates of a Hydrated H_2O Molecule in Alkali Metal Ions at 25 °C

Ion	$(R_1)_{^{17}O}^+/(R_1)_{^{17}O}^0$	$(R_1)_{^{17}O}^+$ / s^{-1}	$(R_1)_H^+/(R_1)_H^0$ a)	$(R_1)_H^+$ / s^{-1}	$(R_1)_{HH}^{+,\text{intra}}$ b) / s^{-1}	$(R_1)_{HH}^{+,\text{intra}}$ c) / s^{-1}	$(R_1)_{OH}^{+,\text{intra}}$ d) / s^{-1}
Li$^+$	1.55	214	2.34	0.658	0.408	0.283	0.626
Na$^+$	1.30	179	1.72	0.484	0.300	0.208	0.460
K$^+$	0.949	131	0.843	0.237	0.147	0.102	0.225
Cs$^+$	0.775	107	0.779	0.219	0.136	0.094	0.209
Pure water		138		0.281	0.174	0.121	0.267

a) $(R_1)_H^+/(R_1)_H^0=(R_1)_{HH}^{+,\text{intra}}/(R_1)_{HH}^{0,\text{intra}}=(R_1)_{OH}^{+,\text{intra}}/(R_1)_{OH}^{0,\text{intra}}$. b) The calculated values by using $0.62\times(R_1)_H^+$ in Ref. 4. c) The calculated values by using $0.43\times(R_1)_H^+$ in Refs. 6 and 10. d) The calculated values by using $0.95\times(R_1)_H^+$ in Refs. 6 and 10.

where γ_{H} is the proton gyromagnetic ratio, $\hbar$ Planck's constant divided by 2π, r_{HH} the intraproton distance of the water molecule, and $\tau^{\pm}_{\mathrm{HH}}$ the reorientational correlation time for the intramolecular ^{1}H–^{1}H axis.

The intramolecular contribution of the ^{1}H–^{17}O dipolar interaction is given by

$$(R_1)^{\pm,\mathrm{intra}}_{\mathrm{OH}} = \frac{35}{3}\frac{\gamma^2_{\mathrm{H}}\gamma^2_{^{17}\mathrm{O}}\hbar^2}{r^6_{\mathrm{OH}}}\tau^{\pm}_{\mathrm{OH}}, \tag{9}$$

where $\gamma_{^{17}\mathrm{O}}$ is the oxygen gyromagnetic ratio, r_{OH} the interdistance between the oxygen and the proton of the water molecule, and $\tau^{\pm}_{\mathrm{OH}}$ the reorientational correlation time for the intramolecular ^{1}H–^{17}O axis. The ^{17}O ($I=5/2$) relaxation is determined intramolecularly by quadrupolar interactions; the rate is give by

$$(R_1)_{^{17}\mathrm{O}} = \frac{3}{135}\left(\frac{e^2qQ}{\hbar}\right)^2\left(1+\frac{\eta^2}{3}\right)\tau_{^{17}\mathrm{O}}, \tag{10}$$

where e^2q is the electric field gradient at the nucleus, Q the electric quadrupole moment of the nucleus, η the asymmetry parameter, and $\tau_{^{17}\mathrm{O}}$ the correlation time for the reorientational of the oxygen electric field gradient tensor (perpendicular axis to the H_2O molecular plane). From Eqs. 3 and 10, the following relation is derived:

$$\frac{(R_1)_{^{17}\mathrm{O}}}{(R_1)^0_{^{17}\mathrm{O}}} = 1 + \left\{x^+\left(k^+\frac{\tau^+_{^{17}\mathrm{O}}}{\tau^0_{^{17}\mathrm{O}}} - 1\right) + x^-\left(k^-\frac{\tau^-_{^{17}\mathrm{O}}}{\tau^0_{^{17}\mathrm{O}}} - 1\right)\right\} \tag{11}$$

and

$$k^{\pm} = \{(e^2qQ/\hbar)^{\pm}/(e^2qQ/\hbar)^0\}^2, \tag{12}$$

where $\tau^0_{^{17}\mathrm{O}}$, $\tau^+_{^{17}\mathrm{O}}$, and $\tau^-_{^{17}\mathrm{O}}$, are the correlation times of pure H_2O and H_2O in the hydration sphere of a cation and an anion, respectively. Here, $k=1$ is for the case when the e^2qQ of hydrated water molecules in cations equals that of pure water molecules; and $k=0.82$ is the correction value reported by van der Maarel et al.,[9] i.e., the e^2qQ value is about 10% smaller than that of pure water molecules. Table 4 shows the three reorientational correlation times of pure and hydrated H_2O molecules for alkali metal ions calculated by two assumptions at 25 °C. One is that the three parameters (r_{HH}, r_{OH}, and k) of hydratd water molecules equal that of pure H_2O molecules; the other equals the correction values reported by van der Maarel et al.[9] From those results, it is clarified that the reorientational correlation time ($\tau^+_{\mathrm{HH}}=\tau^+_{\mathrm{OH}}$) for two parallel axes to the H_2O molecular plane is the same values for each cation within the experimental error. Therefore, the reorientational motion of these two axes is isotropic.

Table 5 shows the anisotropy ($\tau^+_{\mathrm{HH}}/\tau^+_{^{17}\mathrm{O}}$ or $\tau^+_{\mathrm{OH}}/\tau^+_{^{17}\mathrm{O}}$) and the solvent isotope effects for the reorientational motion of hydrated H_2O molecules for alkali metal ions in a dilute aqueous solution. The τ^+_{OH} and τ^+_{D} values are the reorientational correlation times for the intramolecular ^{1}H–^{17}O axis and O–D axis, respectively. Consequently, these two reorientational correlation times give information concerning the reorientational motion of the similar axis (^{1}H–^{17}O axis and O–D axis). The reorientational motion of a hydrated H_2O molecule in alkali metal bromide solutions is anisotropic, similar to the tendency of a hydrated D_2O molecule. That is, for a hydrated H_2O molecule of positive hydration of Li^+ and Na^+ ions, the reorientational motion of the perpendicular axis to the H_2O molecular plane ($\tau^+_{^{17}\mathrm{O}}$) is faster than the reorientational

Table 4. Reorientational Correlation Times of a Hydrated H_2O Molecule and Pure Water at 25 °C[a)]

Ion	τ^+_{HH}[b)]		τ^+_{OH}[b)]		$\tau^+_{^{17}\mathrm{O}}(H_2O)$	
	ps		ps		ps	
Li^+	4.53	4.83	4.54	4.81	2.90	3.54
Na^+	3.36	3.58	3.34	3.54	2.43	2.96
K^+	1.64	1.75	1.63	1.73	1.77	2.16
Cs^+	1.52	1.62	1.50	1.59	1.45	1.77
Pure water	1.96		1.93		1.87	

a) The values of left sides are the calculated by using the parameters (r_{HH}=0.1549 nm, r_{OH}=0.098 nm, and k=1.00) of pure water molecule. The values of right sides are calculated values by using the parameters (r_{HH}=0.1566 nm, r_{OH}=0.099 nm, and k=0.82). b) Calculated from $(R_1)^{+\,\mathrm{b)}}_{\mathrm{HH}}$ and $(R_1)^{+\,\mathrm{c)}}_{\mathrm{OH}}$ values in Table 3.

Table 5. Reorientational Anisotropy and Solvent Isotope Effect on the Reorientational Correlation Time of a Hydrated H_2O Molecule and Pure Water at 25 °C[a)]

Ion	$\tau^+_{\mathrm{OH}}/\tau^+_{^{17}\mathrm{O}}$		$\tau^+_{\mathrm{D}}/\tau^+_{^{17}\mathrm{O}}$[b)]	$\tau^+_{\mathrm{D}}(D_2O)/\tau^+_{\mathrm{OH}}(H_2O)$[b)]		$\tau^+_{^{17}\mathrm{O}}(D_2O)/\tau^+_{^{17}\mathrm{O}}(H_2O)$[b)]	$\dfrac{\tau^+_{\mathrm{OH}}/\tau^+_{^{17}\mathrm{O}}}{\tau^+_{\mathrm{D}}/\tau^+_{^{17}\mathrm{O}}}$	
Li^+	1.57	1.36	1.12	1.04	1.20	1.45	0.72	0.82
Na^+	1.37	1.20	1.13	1.04	1.23	1.27	0.82	0.97
K^+	0.92	0.80	0.89	1.20	1.38	1.24	0.96	1.11
Cs^+	1.03	0.90	0.92	1.11	1.28	1.24	0.89	1.03
Pure water	1.03		1.00	1.23		1.27	0.97	

a) The values of left sides are calculated by using the parameters (r_{HH}=0.1549 nm, r_{OH}=0.098 nm, and k=1.00) of pure water molecule. The values of right sides are calculated by using the parameters (r_{HH}=0.1566 nm, r_{OH}=0.099 nm, and k=0.82). The $\tau^+_{\mathrm{D}}/\tau^+_{^{17}\mathrm{O}}$ and $\tau^+_{^{17}\mathrm{O}}(D_2O)/\tau^+_{^{17}\mathrm{O}}(H_2O)$ values are the same for each k. b) D_2O data are from Ref. 11.

motion of the intramolecular ^1H–^1H and ^1H–^{17}O axes. The reorientational anisotropies for the negative hydration of K^+ and Cs^+ ions are vice versa. The reorientational anisotropy of a H_2O molecule around the positive hydration ions, especially for the Li^+ ion, is larger than that of a D_2O molecule, in spite of the anisotropy of H_2O molecules around the negative hydration ions is almost the same order of a D_2O molecule.

As shown the last column in Table 5, we can observe the large solvent isotope effect on the reorientational anisotropy of a water molecule in the Li^+ hydration sphere. The reasons may be explained by comparing the solvent isotope effect on the reorientational correlation times within the hydration sphere with the effect on the correlation times in water molecules having a bulk water structure. Our results for the ^2D and ^{17}O isotope effects on the reorientational correlation times of a pure water molecule ($\tau_{\mathrm{D}}^{+}(D_2O)/\tau_{\mathrm{OH}}^{+}(H_2O)=1.23$ and $\tau_{^{17}\mathrm{O}}^{+}(D_2O)/\tau_{^{17}\mathrm{O}}^{+}(H_2O)=1.27$) are in good agreement with the ^2D isotope effect on the reorientational correlation time obtained by Lankhorst et al. ($\tau(D_2O)/\tau(H_2O)=1.28$)[6)] and some related dynamical properties, such as the self-diffusion (($D(H_2O)/D(D_2O)=1.23$)[17)] and viscosity ($\eta(D_2O)/\eta(H_2O)=1.23$).[13)] The solvent isotope effects on the reorientational correlation times in negative hydration water molecules (calculated assuming pure water parameters (r_{HH}, r_{OH}, and e^2qQ)), are almost of the same order as that of the isotope effects on the reorientational correlation times in pure water molecules. The solvent isotope effects on the reorientational correlation time of ^1H and ^{17}O nuclei in the positive hydration water of Li^+ ion are remarkable compared with those of a hydration water molecule in the nagetive hydration sphere of another cation and a pure water molecule in water. This isotope effect on the reorientational correlation time of the intermolecular ^1H–^{17}O and ^1H–^1H dipolar interactions is smaller than that of a pure water molecule, and the effect of the ^{17}O nucleus of the hydration water molecule of the Li^+ ion is larger. On the other hand, the solvent isotope effect on the reorientational correlation time of the negative and positive hydration water molecule calculated by using the correction values are of the same order in pure water, except for that of ^{17}O nucleus. The solvent isotope effect on the ^{17}O nucleus of the hydrated water molecule of the Li^+ ion is enhanced to be 1.45. It is natural that the ^1H–^1H, ^1H–^{17}O distance, and the quadrupole coupling constant of water molecules in the hydration sphere change with respect to pure water.[9)] Therefore, the solvent isotope effect by using the correction values may give a true value; thus, the ^{17}O nuclei of the hydrated water molecule of the Li^+ ion only shows a different large solvent isotope effect against that of a pure water molecule. The hydrated water molecule of the Li^+ cation is orientated with their oxygen atom pointing towards the ion, and the Li^+ ion has the largest surface charge density among the univalent cations. Consequently, H_2O molecules around the Li^+ ion are strongly hydrated, so that the largest solvent isotope effect is observed on the ^{17}O nucleus of a hydrated water molecule of the Li^+ ion.

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