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NMR Studies on the Rotational Motion of Coordinated D_2O Molecules in MBr ($M=Li^+$, Na^+, K^+, Cs^+) Dilute Aqueous Solutions

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The parallel (D,$\tau_{//}$) and perpendicular (^{17}O,$\tau_{\perp}$) rotational correlation times of coordinated D_2O molecules in MBr ($M=Li^+$, Na^+, K^+, Cs^+) aqueous solutions in the concentration range of 0.2 to 1.0 mol kg^{-1} at 25 °C were determined by NMR. The spin-lattice relaxation rates (R_1) varied linearly with increase in concentration up to 1.0 mol kg^{-1}. The ratios ($\tau_{//}/\tau_{\perp}$) of the rotational correlation times of coordinated D_2O molecules in Li^+, Na^+, K^+, and Cs^+ ions were 1.12, 1.13, 0.89, and 0.92, respectively. These results indicate that for coordinated D_2O molecules in Li^+ and Na^+ ions, the perpendicular rotational motion is 10% faster than the parallel one. On the other hand, for coordinated D_2O molecules in K^+ and Cs^+ ions, the tendency was reversed. These results are explained in terms of both the Eulerian angle β between the diffusion tensors with the molecular plane and the intermolecular interactions between the ions and D_2O molecules.

In general, ion-water and ion-ion interactions are coupled in real electrolyte solutions. Study of concentration effect on dilute aqueous electrolyte solutions is of importance to the understanding of the translational and rotational dynamics of ions and water molecules, because studies of dilute solutions give us information about accurate limiting values due only to physical properties of ion-water interactions at infinite dilution. There are two approaches to investigate the dynamics of electrolyte solutions. One is by using dynamical properties of ions as solutes and the other by using properties of water molecules as a solvent in electrolyte solutions. This study focuses on the rotational dynamics of water molecules as a solvent in dilute electrolyte solutions. For the translational motion of water molecules, the viscosity B-coefficients[1] due to ion-water interactions have been established for concentrations below 0.1 mol dm^{-3}.[2] Studies of the rotational motion of water molecules at low electrolyte concentrations less than 1.0 mol kg^{-1} are lacking compared with those of the translational motion except for the D magnetic relaxation studies by Uedaira and Uedaira.[3] Therefore, study of the concentration effect on the rotational motion of water molecules in dilute electrolyte solutions is necessary to understand the whole picture of the rotational dynamics of water molecules in electrolyte solutions.

Many studies of the rotational motion of water molecules in electrolyte solutions have been done by use of NMR.[4] Hertz et al.[5—8] studied the concentration dependence of spin-lattice relaxation rates (R_1) of ^{1}H and ^{17}O nuclei of coordinated water molecules in electrolyte solutions in the concentration range of 1 to 6 mol kg^{-1}. They calculated spin-lattice relaxation times (T_1) of ^{17}O nucleus of natural abundance in water molecules from the half width of signal with a large error. These data were expressed by a quadratic polynomial equation as a function of molality concentration to provide relaxation rates of coordinated water for each ion at infinite dilution. Since ^{1}H nucleus (spin quantum number $I=1/2$) is relaxed by the dipole-dipole interaction, observed R_1 values contribute to the intermolecular (translational motion) in addition to the intramolecular (rotational motion) interaction. In order to improve the accuracy of rotational relaxation rates of coordinated water molecules in electrolyte solutions, Leyte et al.[9—12] studied the concentration dependence of R_1 of D and ^{17}O nuclei of water molecules by the inversion-recovery method in the same concentration range as Hertz et al.[5—8] Both the nuclei are relaxed by the quadrupole interaction due to the pure rotational motion of water molecules. They first reported the concentration dependence of the anisotropy of the rotational motion of water molecules in the hydration sphere. In a range of high electrolyte concentrations, the relative D and ^{17}O relaxation rates crossed at 4 mol kg^{-1} for water molecules in the hydration sphere of Li^+ ion, and for Na^+ ion at about 1.0 mol kg^{-1}. However, the relative D and ^{17}O relaxation rates of K^+ or Cs^+ did not change in the whole experimental concentration range of 1—5 mol kg^{-1}.

We can point out the following disadvantage of the above two experiments at the high concentration range above 1.0 mol kg^{-1} involving ion-ion interactions. In order to consider the rotational motion of water molecules at infinite dilution, experiments at low concentrations below 1.0 mol kg^{-1} are important to treat the ion-water (dipole) interaction separately, if one wants to clarify the quantitative rotational dynamics of coordinated water molecules in aqueous electrolyte solutions. Relevant experiments should be done at concentrations below 1.0 mol kg^{-1}. Since R_1 varies linearly with concentration below 1.0 mol kg^{-1}, both the ion-ion and the coordination sphere interaction can be neglected. Therefore, we can consider the rotational dynamics of water molecules quantitatively, solely from the view point of ion-water dipole interaction on the basis of the two-state model.

The NMR technique recently developed is preferable for studying the rotational motion of water molecule at lower concentrations in aqueous electrolyte solution to any other available experimental techniques. For D_2O molecules, there are two nuclei, D and ^{17}O, which can be measured by NMR, and the rotational motion of water molecules is derived from spin-lattice relaxation rate (R_1) values.

In the present paper, we report the concentration dependence of the relaxation rate of D and ^{17}O nuclei of coordinated D_2O molecules in alkali metal (Li^+, Na^+, K^+, Cs^+) bromide aqueous solutions up to 1.0 mol kg^{-1}. The main component of the quadrupole interaction tensor at D nucleus lies along the O-D bond, and the component at ^{17}O nucleus is perpendicular to the molecular plane of water. The two characteristic rotational motions of D and ^{17}O nuclei are the parallel and the perpendicular rotational motion on the water molecular plane. Consequently, comparing the D relaxation rate with that of ^{17}O, we can see which of the positive and the negative hydration reflects the componential rotational motion. Furthermore, the anisotropic rotational motion of D_2O molecules coordinated to alkali metal ions can be determined by using D and ^{17}O relaxation rates and on the basis of the two-state model. We discuss the ion-D_2O interaction or hydration of alkali metal ions from the viewpoint of anisotropic rotational motion of D_2O molecule.

Experimental

Samples. Alkali metal bromide (LiBr, NaBr, KBr, CsBr) salts from Nakarai Tesque, Inc. (extra pure grade) were recrystallized from water or ethanol. D_2O was obtained from CEA, containing D over 99.8%. Sample solutions were passed through membrane filters with a pore size of 0.1 μm to remove dusts. Sample solutions were bubbled with nitrogen gas for about five minutes just before NMR measurement to remove oxygen gas.

NMR Measurement. D and ^{17}O relaxation times were measured on a JEOL GX-270 pulsed spectrometer, operating at 41.5 and 36.6 MHz, respectively. Samples were kept in 10 mm diameter glass tubes. Resolution was established by D nucleus of neat D_2O before sample measurement. Spin-lattice relaxation times (T_1) were measured by the inversion-recovery method, using a pulse sequence of 180°-t-90° pulse. T_1 values were determined for each sample at 16 different time intervals (t), and the pulse delay time (PD) was more than $10T_1$. Frequencies were 1200 Hz for D nucleus and 60000 Hz for ^{17}O nucleus. The free induction decay of D and ^{17}O nuclei was accumulated 4 to 16 times and 100 to 1600 times, respectively, depending on concentration. The error in T_1 measurement was less than 2%. Temperature was controlled to 25±0.1 °C with an air compressor.

Results and Discussion

Concentration Dependence of R_1 of D_2O Molecule in Aqueous Bromide Solutions. The relation between the spin-lattice relaxation rates ($R_1=1/T_1$) of the D and ^{17}O nuclei of a D_2O molecule and their concentration in aqueous bromide solutions at 25 °C is shown in Figs. 1 and 2, and Table 1. 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 values of D and ^{17}O nuclei are in the order

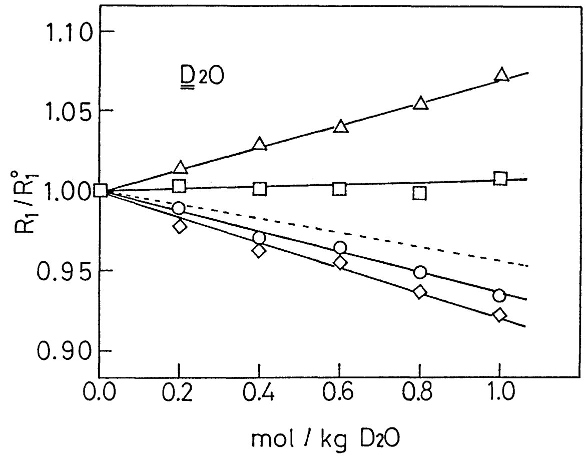

Fig. 1. Plots of D relaxation rates (R_1/R_1^0) of a D_2O molecule in alkali metal bromides solutions at 25 °C.
△: LiBr, □: NaBr, ○: KBr, ◇: CsBr, ------: KCl.

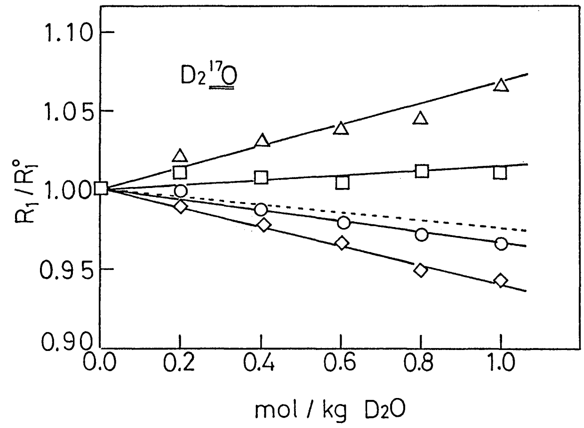

Fig. 2. Plots of ^{17}O relaxation rates (R_1/R_1^0) of a D_2O molecule in alkali metal bromides solutions at 25 °C.
△: LiBr, □: NaBr, ○: KBr, ◇: CsBr, ------: KCl.

Table 1. D and ^{17}O Spin-Lattice Relaxation Rates (R_1)[a] of a D_2O Molecule[b] at 25 °C

Salt	[D$_2$O]/mol kg^{-1} 0.2		0.4		0.6		0.8		1.0	
	D	^{17}O	D	^{17}O	D	^{17}O	D	^{17}O	D	^{17}O
LiBr	2.29	179	2.32	181	2.35	182	2.38	184	2.43	188
NaBr	2.26	177	2.26	176	2.26	176	2.25	178	2.27	177
KBr	2.22	175	2.18	172	2.16	171	2.13	170	2.10	169
CsBr	2.20	173	2.18	172	2.15	169	2.11	166	2.09	165
KCl	2.26	174	2.25	173	2.20	173	2.21	172	2.17	172

a) Unit is s^{-1} and accuracy is within 2%. b) For pure D_2O molecule, D=2.27 s^{-1} and ^{17}O=176 s^{-1}

$$\mathrm{Li}^+ > \mathrm{Na}^+ > 1 > \mathrm{K}^+ > \mathrm{Cs}^+.$$

It is clear that the positive hydration ions (Li^+, Na^+) cause increase in D and ^{17}O relaxation rates, whereas the negative hydration ions (K^+, Cs^+) cause decrease in the relaxation rates.

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

$$R_1^{\mathrm{obs}} = (1+B_{\mathrm{D}}c)R_1^0 \tag{1}$$

for D nucleus, and

$$R_1^{\mathrm{obs}} = (1+B_{\mathrm{O}}c)R_1^0 \tag{2}$$

for ^{17}O nucleus, where, R_1^{obs} and R_1^0 are the spin-lattice relaxation rates at concentration c and for pure D_2O, respectively.

Since B_{D} and B_{O} contain contributions of cation (+) and anion (−), $B_{\mathrm{D}} = B_{\mathrm{D}}^+ + B_{\mathrm{D}}^-$ and $B_{\mathrm{O}} = B_{\mathrm{O}}^+ + B_{\mathrm{O}}^-$ Eqs. 1 and 2 are transformed to

$$R_1^{\mathrm{obs}} = \{1+(B_{\mathrm{D}}^+ + B_{\mathrm{D}}^-)c\}R_1^0 \tag{3}$$

for D nucleus, and

$$R_1^{\mathrm{obs}} = \{1+(B_{\mathrm{O}}^+ + B_{\mathrm{O}}^-)c\}R_1^0 \tag{4}$$

for ^{17}O nucleus, where B_{x}^+(x=D or O) and B_{x}^- values are determined by the following method. First, on the assumption that $B_{\mathrm{x}}^+ = B_{\mathrm{x}}^-$ is established for KCl solution in the case of equal splitting of B-coefficient into ionic components, $B_{\mathrm{x}}^-(\mathrm{Br}^-)$ values are determined by using $B_{\mathrm{x}}^{\mathrm{obs}}$ of KBr solution and $B_{\mathrm{x}}^+(\mathrm{K}^+)$. Next, from $B_{\mathrm{x}}^-(\mathrm{Br}^-)$ and $B_{\mathrm{x}}^{\mathrm{obs}}$ of various electrolyte solutions, B_{x}^+ values for various aqueous bromide solutions are determined.

B_{D}, B_{O}, B_{D}^+, B_{O}^-, and $B_{\mathrm{D}}^+ - B_{\mathrm{O}}^+$ values are shown in Table 2. For Li^+, Na^+, K^+, and Cs^+ ions, the $B_{\mathrm{D}}^+ - B_{\mathrm{O}}^+$ values are 0.03, 0.02, −0.01, and −0.01, respectively. From these results, it is clear that the structure-making effect of Li^+ and Na^+ ions or the structure-breaking effect of K^+ an Cs^+ ions is more influenced by the rotational motion of D nucleus than by that of ^{17}O nucleus up to 1.0 mol kg^{-1}.

Anisotropic Rotational Motion of the Coordinated Water Molecules. R_1^{obs} values vary linearly with increasing concentration for all salts, as shown in Figs. 1 and 2. By assuming that R_1^{obs} is the sum of the spin-lattice relaxation rates of bulk water (R_1^0), the anion coordinated (R_1^-) and cation coordinated (R_1^+) water molecules are given by[5,7)]

$$R_1^{\mathrm{obs}} = (1-x^+-x^-)R_1^0 + x^-R_1^- + x^+R_1^+, \tag{5}$$

$$R_1^{\mathrm{obs}}/R_1^0 = 1 + x^-\{R_1^-/R_1^0 - 1\} + x^+\{R_1^+/R_1^0 - 1\}, \tag{6}$$

$$x^- = n^-c/50.0 \quad x^+ = n^+c/50.0,$$

where R_1^0, R_1^+, R_1^-, n^+, and n^- are the spin-lattice relaxation rates of pure water, cation coordinated water, and anion coordinated water and the coordination numbers of cation and anion, respectively. In this study, we use $n^+ = n^- = 6$ for all ions.[5)] In Eq. 6, on the assumption that $R_1^+ = R_1^-$ is established for KCl solution in the case of equal splitting of B-coefficient into an ionic component,[13)] R_1^+ values for various ions are determined by the same method from B^+ values. From the fact that R_1^{obs} varies linearly with increasing concentration, it is clear that R_1^+ and R_1^- values do not vary at concentrations up to 1.0 mol kg^{-1}. The R_1^+ and R_1^- values of D and ^{17}O nuclei are shown in Table 3.

D and ^{17}O nuclei are quadrupole nuclei with spin quantum numbers I=1 and 5/2, respectively. These

Table 3. D and ^{17}O Spin-Lattice Relaxation Rates ($R_1^{\pm}$)[a)] of Coordinated D_2O Molecules of Infinitely Diluted Complexes at 25 °C

Ion	$R_1^{\pm}$(D)/s^{-1}	$R_1^{\pm}$(^{17}O)/s^{-1}
Li^+	4.51	312
Na^+	3.33	228
K^+	1.87	163
Cs^+	1.59	134
Br^-	1.40	136
Cl^-	1.87	163

a) Accuracy is within 4%.

Table 2. B_{D}, B_{O}, B_{D}^+, B_{O}^+, and $B_{\mathrm{D}}^+ - B_{\mathrm{O}}^+$ Values[a)] at 25 °C

Salt	B_{D}[b)]	B_{O}[b)]	B_{D}^+	B_{O}^+
LiBr	0.065±0.003 (0.102±0.008)	0.058±0.002 (0.072±0.009)	0.106±0.005	0.082±0.004
NaBr	0.010±0.001 (0.05 ±0.01)	0.010±0.001 (0.022±0.008)	0.051±0.001	0.035±0.001
KBr	−0.060±0.002 (−0.027±0.003)	−0.032±0.0008 (−0.021±0.001)	−0.019±0.002	−0.008±0.0002
CsBr	−0.074±0.002 (−0.041±0.003)	−0.047±0.001 (−0.030±0.005)	−0.033±0.002	−0.023±0.001
	$B_{\mathrm{D}}^+ - B_{\mathrm{O}}^+$			
LiBr	0.03 ±0.02			
NaBr	0.02 ±0.01			
KBr	−0.014±0.008			
CsBr	−0.01 ±0.01			

a) Concentration is reduced to mol kg^{-1} (55.5 D_2O) which can correspond to H_2O. b) ( ) indicates citation of Cl salt values from Ref. 12.

nuclei relax mainly by electric quadrupole interaction. In this case, the relation between spin-lattice relaxation rate (R_1) and rotational correlation time (τ) is given by[14]

$$R_1^{\text{obs}} = \frac{3}{400}\,\frac{2I+3}{I^2(2I-1)}\left(\frac{e^2qQ}{\hbar}\right)^2\left(1+\frac{\eta^2}{3}\right)\left[\frac{2\tau}{1+(\pi\nu\tau)^2}+\frac{8\tau}{1+(2\pi\nu\tau)^2}\right], \tag{7}$$

where I, η, $e^2qQ/\hbar$, and ν are quantum number, asymmetry parameter, quadrupole coupling constant, and resonance frequency of experiment, respectively. For the experimental condition of motional narrowing limit ($2\pi\nu\tau \ll 1$), Eq. 7 is transformed to

$$R_1^{\text{obs}} = \frac{3}{40}\,\frac{2I+3}{I^2(2I-1)}\left(\frac{e^2qQ}{\hbar}\right)^2\left(1+\frac{\eta^2}{3}\right)\tau. \tag{8}$$

When Eq. 8 is substituted into Eq. 6, we obtain[8]

$$R_1^{\text{obs}} = \frac{3}{40}\,\frac{2I+3}{I^2(2I-1)}\left[(1-x^+-x^-)\left(\frac{e^2qQ}{\hbar}\right)_0^2\left(1+\frac{\eta^2}{3}\right)\tau^0 + x^+\left(\frac{e^2qQ}{\hbar}\right)_+^2\left(1+\frac{\eta^2}{3}\right)\tau^+ + x^-\left(\frac{e^2qQ}{\hbar}\right)_-^2\left(1+\frac{\eta^2}{3}\right)\tau^-\right]. \tag{9}$$

Assuming $(e^2qQ/\hbar)_0=(e^2qQ/\hbar)_+=(e^2qQ/\hbar)_-$[5,8] and using the constant values for D ($e^2qQ/\hbar=254$ kHz with $\eta=0.135$) and for ^{17}O ($e^2qQ/\hbar=8.1$ MHz with $\eta=0.75$)[11] for this experiment, we may evaluate τ^+ and τ^- from Eqs. 6 and 9.

The rotational motion of quadrupole nuclei is concerned with reorientation of the main component of quadrupole interaction tensor. The main component of the ^{17}O nucleus in D_2O molecule lies along the axis perpendicular to the molecular plane, and the D nucleus does almost along the O-D bond axis.[11,15,16] The characteristic rotational motion of D and ^{17}O nuclei are the parallel and the perpendicular rotational motion of the D_2O molecular plane. From this point of view, we can adapt $\tau_{/\!/}$ (the parallel rotation for the molecular plane)$=\tau^+$ (D) and $\tau_\perp$ (the perpendicular rotation for the molecular plane)$=\tau^+(^{17}O)$.

Table 4 shows the $\tau_{/\!/}$ and $\tau_\perp$ values for each ion, which are independent of concentration for dilute electrolyte solutions below 1.0 mol kg^{-1}. Since the $\tau_{/\!/}$ and $\tau_\perp$ values for a pure D_2O molecule are 2.38 and 2.37 ps, respectively, it is concluded that the rotational motion of a pure D_2O molecule is isotropic. The rotational anisotropies ($\tau_{/\!/}/\tau_\perp$) of the coordinated D_2O molecules of alkali metal ions (Li^+, Na^+, K^+, Cs^+) are 1.12, 1.13, 0.89, and 0.92, respectively. These results tell us that for the coordinated D_2O molecules of Li^+ and Na^+ ions, the perpendicular rotation is 10% faster than the parallel one on the D_2O molecular plane. On the other hand, for the coordinated D_2O molecules of K^+ and Cs^+, the perpendicular rotation is about 10% slower than the parallel one. This fact is interesting to understand the dynamic aspect of the rotational motion of the positive (Li^+ and Na^+) and negative (K^+ and Cs^+) hydrated D_2O molecules at infinite dilution.

Table 4. Rotational Correlation Times (τ) of Coordinated D_2O Molecules of Infinitely Diluted Complexes and Pure Water at 25 °C

Ion	D[a]	^{17}O[a]	D/^{17}O[b]
	$\tau_{/\!/}$/ps	$\tau_\perp$/ps	$\tau_{/\!/}/\tau_\perp$
Li^+	4.72	4.22	1.12
Na^+	3.49	3.09	1.13
K^+	1.96	2.20	0.89
Cs^+	1.67	1.81	0.92
pure D_2O	2.38	2.37	1.00

a) Accuracy is within 4%. b) Accuracy is within 8%.

The Eulerian angle β between the diffusion tensors with the molecular plane is important to discuss the anisotropic rotational motion of coordinated D_2O molecules. For the experimental condition of motional narrowing limit, the rotational correlation time is transformed to[9]

$$\tau_x^+ = \frac{1}{\sum_{k=-2}^{2}|V_k^{(2)}|^2}\sum_{k,l,m=-2}^{2} V_k^{(2)}V_l^{(2)*}D_{kl}^{(2)}(\beta)D_{lm}^{(2)*}\tau_m, \tag{10}$$

$$\tau_m^{-1} = 6D_\perp + m^2(D_{/\!/}-D_\perp), \tag{11}$$

where $D_{km,ln}^{(2)}$ is the Wigner matrix elements describing the diffusion tensor which is characterized by the Eulerian angle β, $D_{/\!/}$ and $D_\perp$ are the diffusion component on the molecular plane which bisects the D-O-D angle and the perpendicular diffusion component for $D_{/\!/}$, respectively, and $V_{k.l}^{(2)}$ is the irreducible elements.

For D and ^{17}O nuclei, $V_0^{(2)}=eq(3/2)^{1/2}$ and $V_{+2}^{(2)}=-\eta/2$, and the asymmetry parameter η is defined as $\eta=(V_{yy}-V_{xx})/V_{zz}$. From this relation, Eq. 10 is transformed to[11]

$$\tau_x^+ = \sum_{m=0}^{2} a_m^x\tau_m, \tag{12}$$

where a_m^x is the normalized constant defined by β. With the experimental $\tau_D^+/\tau_O^+(=\tau_{/\!/}/\tau_\perp)$ value, the Eulerian angle β and diffusion tensor $D_{/\!/}/D_\perp$ are defined theoretically by Eqs. 10—12. From these calculations, the relation $\tau_{/\!/}/\tau_\perp>1$ is found in the range $0°<\beta<30°$, whereas $\tau_{/\!/}/\tau_\perp<1$ when $\beta>40°$. From comparison of the theoretical treatment and our experimental results, for Li^+ and Na^+ ions β is between 0° and 30°, and for K^+ and Cs^+ ions β is larger than 40° at infinite dilution from the linear relation between R_1 and concentration in the low concentration range below 1.0 mol kg^{-1}. The β values for each ion are independent of salt concentration. Therefore, the limiting values at infinite dilution reflect the relaxation behavior of isolated hydration complex. At high concentrations above 1.0 mol kg^{-1} studied by van der Maarel et al.[12] for Li^+ ion the relative D and ^{17}O relaxation rates cross in the 4 mol kg^{-1} range, where β increases from $\beta<30°$ at lower concentrations to $\beta>40°$ at higher concentrations. For Na^+ ion β is found to be larger than 40° above 1—2 mol kg^{-1} and may be less than 30° at infinite dilution. For K^+ and Cs^+, $\beta>40°$ in the whole concentration range 1—5 mol kg^{-1}.

We can describe the whole picture of the Eulerian angle β between an ion and a water molecule. For K^+ and Cs^+, β keeps being a constant larger than 40° in the whole concentration range from 5 mol kg^{-1} to infinite dilution. The angle for the negative hydration ions is not influenced by the ion-ion interaction. On the other hand, for Li^+ and Na^+, the orientation of water molecules of the isolated hydrated complex at infinite dilution perturbs with increasing concentration, which increases from $\beta<30°$ at lower concentrations to $\beta>40°$ at higher concentrations with the electric field at the ionic surface. Therefore, we can not distinguish in dynamic properties between the positive and negative hydration ions from β values at higher concentrations. Only at infinite dilution, it is possible to find difference in anisotropy between rotational motions of coordinated water molecules.

Finally, we consider the reason why the anisotropy of the rotational motion of coordinated D_2O molecules occurs in electrolyte solutions. The coordinated D_2O molecules in the positive hydration ions (Li^+, Na^+) are very strongly hydrated with D_2O (oxygen-metal ion bonding) but not in a rigid arrangement. D_2O molecules deviate β degrees from the plane of the ion-D_2O complex (Fig. 3).[17,18] The perpendicular rotation of this structure is freer than the parallel rotation. Since the structure changes easily from $+\beta$ to $-\beta$ degrees, $\tau_{//}$ must be larger than $\tau_{\perp}$.

On the other hand, for the small surface-charge-density ions K^+ and Cs^+, the D_2O-D_2O bonds are stronger than the ion-D_2O bonds, compared with Li^+ and Na^+ ions. In this case, one coordinated D_2O molecule of K^+ and Cs^+ ions forms three D_2O-D_2O hydrogen bonds and one ion-D_2O bond. For these four bonds, the hydrogen bonds in the D_2O molecular plane lie along the bonding direction and the other bonds lie above the hydrogen bonds of pure D_2O because the rotational correlation times decrease with increasing concentration. The rotational motion of the coordinated D_2O molecules of the ions is caused by breaking these bonds. Four bonds among D_2O molecules and ions must be broken for the perpendicular rotation, but three bonds need to be broken for the parallel rotation. This is the reason why $\tau_{\perp}$ is larger than $\tau_{//}$.

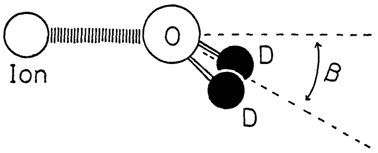

Fig. 3. The stereo formula of ion-coordinated D_2O molecule complex.

Conclusion

The spin-lattice relaxation rates (R_1) vary linearly with increasing concentration up to 1.0 mol kg^{-1}. The linear slope of the concentration dependence of R_1 of ^{17}O is smaller than that of D for Li^+ and Na^+ ions. On the other hand, K^+ an Cs^+ ions show the reverse tendency. These results tell us that the positive and negative hydration effects on R_1 are more significant for the D nucleus than for the ^{17}O nucleus.

The anisotropy ($\tau_{//}/\tau_{\perp}$) of the coordinated D_2O molecules at infinite dilution is 1.12, 1.13, 0.89, and 0.92 for Li^+, Na^+, K^+, and Cs^+ ions, respectively. For the coordinated D_2O molecules in the positive hydration ions, the perpendicular rotational motion is about 10% faster than the parallel one. On the other hand, the parallel rotational motion of the coordinated D_2O molecules in the negative hydration ions is 10% faster than the perpendicular one. These dynamic properties relate to the difference in bonding strength between the D_2O-ion or D_2O-D_2O interactions.

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References

1) G. Jones and M. Dole, *J. Am. Chem. Soc.*, **51**, 2950 (1929).

2) D. Eagland and G. Pilling, *J. Phys. Chem.*, **76**, 1902 (1972).

3) H. Uedaira and H. Uedaira, *Nippon Kagaku Kaishi*, **1986**, 1265.

4) K. Miura, K. Hashimoto, H. Fukui, E. Yamada, and S. Shimokawa, *J. Phys. Chem.*, **89**, 5098 (1985).

5) L. Endom, H. G. Hertz, B. Thul, and M. D. Zeilder, *Ber. Bunsen-Ges. Phys. Chem.*, **71**, 1008 (1967).

6) H. G. Hertz, R. Tutsch, and H. Versmid, *Ber. Bunsen-Ges. Phys. Chem.*, **75**, 1177 (1971).

7) G. Engel and H. G. Hertz, *Ber. Bunsen-Ges. Phys. Chem.*, **72**, 808 (1968).

8) F. Fister and H. G. Hertz, *Ber. Bunsen-Ges. Phys. Chem.*, **71**, 1032 (1967).

9) C. W. R. Mulder, J. Schriever, and J. C. Leyte, *J. Phys. Chem.*, **87**, 2336 (1983).

10) C. W. R. Mulder, J. Schriever, W. J. Jesse, and J. C. Leyte, *J. Phys. Chem.*, **87**, 2342 (1983).

11) R. P. W. J. Struis, J. de Bleijser, and J. C. Leyte, *J. Phys. Chem.*, **91**, 1639 (1987).

12) J. R. C. van der Maarel, D. Lankhorst, J. be Bleijser, and J. C. Leyte, *J. Phys. Chem.*, **90**, 1470 (1986).

13) M. Kaminsky, *Discussion Faraday Soc.*, **24**, 171 (1957).

14) A. Abragam, "The Principles of Nuclear Magnetism," Oxford University, Oxford (1967), p. 313.

15) H. W. Spiess, B. B. Garrett, and R. K. Sheline, *J. Chem. Phys.*, **51**, 1201 (1969).

16) D. E. Woessner, *J. Chem. Phys.*, **40**, 2341 (1964).

17) R. W. Impey, P. A. Madden, and I. R. McDonald, *J. Phys. Chem.*, **87**, 5071 (1983).

18) N. Ohtomo and K. Arakawa, *Bull. Chem. Soc. Jpn.*, **52**, 2755 (1979).