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NMR Studies on Reorientational Motion of Hydrated D_2O Molecules of Halaide Ions (F^-, Cl^-, Br^-, and I^-) in Dilute Aqueous Solutions

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The spin–lattice relaxation rates of the D and ^{17}O nuclei of D_2O molecules have been measured for dilute aqueous solutions of potassium halides (KF, KBr, KCl, KI) in the concentration range below 1.0 mol kg^{-1} at 25 °C. The agreement between the B_X' coefficients of the spin–lattice relaxation rate (reorientational motion) and the B$^-$ coefficients of the solution viscosity of the anions is somewhat better than that of the cations. The reorientational motion of hydration for D_2O molecules of Cl^-, Br^-, and I^- ions was anisotropic; this anisotropic motion is enhanced with increasing ion radius. On the other hand, the hydration D_2O molecule of the F^- ion was approximately isotropic.

The concentration effect on the reorientational correlation times of hydrated water molecules in electrolyte solutions is both important and necessary in understanding the dynamic features of ionic hydration. Measurements of the spin–lattice relaxation rate (R_1) have mainly been carried out in the high concentration range above 1.0 mol kg^{-1}.[1-9] These data are expressed by a quadrutic polynominal equation as a function of the concentration in order to provide reorientational correlation times of hydrated water molecules for each ion at infinite dilution. We have recently carried out systematic NMR studies concerning the reorientational correlation times of hydrated water molecules in low the concentration range below 1.0 mol kg^{-1} [10-14] in order to elucidate the ion–water interactions. Since R_1 varies linearly with concentration below 1.0 mol kg^{-1}, each hydration sphere of the ions can be isolated from each other.

It is well known that the dynamic properties of aqueous electrolyte solutions are influenced by the ionic radius as well as the charge of ions. The structure-breaking effect of halide ions on the viscosity of solutions is greater than that of alkali metal ions, since the ionic radius of halide ions is larger than that of alkali metal ions. Studies concerning the dynamic properties of hydrated water molecules of ions have attracted both physical and biochemical attention, since the behavior of water in aqueous electrolyte solutions plays an essential role in biological reactions and protein stability.[15]

A D_2O molecule has a D and an ^{17}O nuclei which relax by a quadrupole interaction. Their spin–lattiice relaxation rates have been measured by NMR. The main component of the quadrupole interaction tensor at the D nuclei lies along the O–D bond axis, and the main component at the ^{17}O nucleus is the perpendicular axis to the molecular plane of a D_2O molecule.[16,17] The reorientational correlation times of the D and ^{17}O nuclei furnish information on the reorientational motion of the O–D axis and the axis perpendicular to the D_2O molecular plain.

In the present study we focused attention on the dynamic properties of the hydration D_2O molecule of halide ions (F^-, Cl^-, Br^-, and I^-) and measured the concentration dependence of the D and ^{17}O spin–lattice relaxation rates of D_2O molecules below 1.0 mol kg^{-1}. Comparing the D relaxation rate with that of the ^{17}O nucleus on the basis of the two-state model, we can discuss the dynamic behavior of a hydrated D_2O molecule.

Experimental

Samples. Potassium halide (KF, KCl, KBr, KI) salts from Nakarai Tesque Inc. (extra pure grade) were recrystallized from water. D_2O obtained from CEA contained over 99.8% of D.

NMR Measurement. The D and ^{17}O relaxation times (T_1) were obtained on a JEOL GX-270 spectrometer operating at 41.5 and 36.6 MHz, respectively. T_1 was measured by using the inversion–recovery method (180°-t-90° pulse sequence). The T_1 values were determined for each sample at 16 different time intervals (t); the pulse delay time was more than $10T_1$. The reproducibility of the T_1 measurements was within 2%. The temperature was controlled to 25±0.1° by a GVT 1 temperature-control unit (JEOL).

Results and Discussion

B_X and B_X' Coefficients. The relation between the R_1/R_1^0 values of the D and ^{17}O nuclei of D_2O molecules in potassium halaide aqueous solutions and their concentrations at 25 °C is shown in Figs. 1 and 2. The slopes of the D and ^{17}O nuclei shown in Figs. 1 and 2 are in the following order:

$$KI < KBr < KCl < 1 < KF.$$

This tendency corresponds to the B-coefficient of the solution viscosity. The R_1/R_1^0 values of the D and ^{17}O nuclei vary linearly with increasing concentration up to 1.0 mol kg^{-1}, in a manner similar to other salts;[10-12] the concentration dependences of R_1/R_1^0 are given by the following equations:

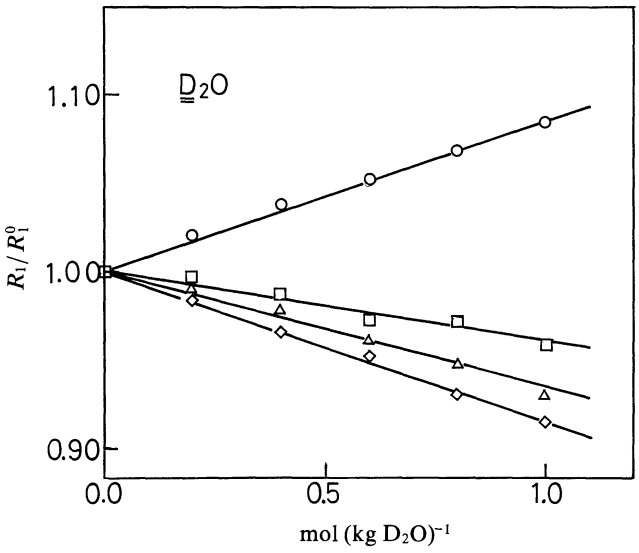

Fig. 1. Plots of D relaxation rates (R_1/R_1^0) of D_2O molecules in potassium halide solutions at 25°C. ○: KF, □: KCl, △: KBr, ◇: KI.

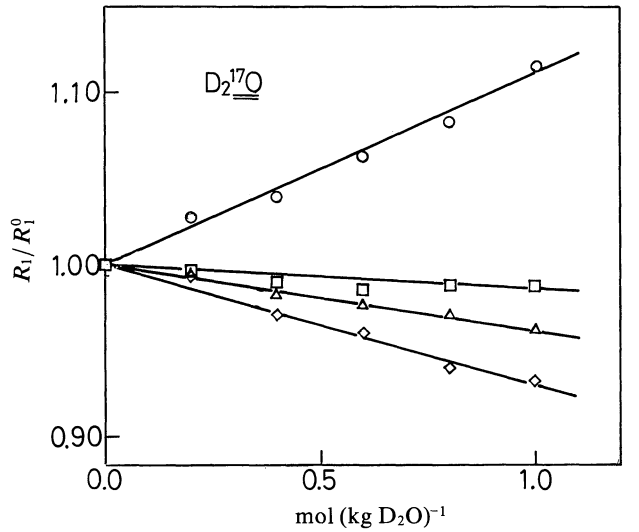

Fig. 2. Plots of ^{17}O relaxation rates (R_1/R_1^0) of D_2O molecules in potassium halide solutions at 25°C. ○: KF, □: KCl, △: KBr, ◇: KI.

$$R_1/R_1^0 = 1 + B_x \cdot m \tag{1}$$

and

$$R_1/R_1^0 = 1 + B_x' \cdot c \quad (x = D \text{ or } {}^{17}O), \tag{2}$$

where R_1 and R_1^0 are the spin–lattice relaxation rates of D_2O molecules at a certain concentration, m (mol kg^{-1}) or c (mol dm^{-3}), and pure D_2O, respectively. The B_X values are separated into contributions from individual ions on the basis of the following conventional assumptions:[18,19]

$$B(KCl) = B^+(K^+) + B^-(Cl^-), \text{ and } B^+(K^+) = B^-(Cl^-). \tag{3}$$

From Eqs. 1 and 3, the following relation is obtained:

$$R_1/R_1^0 = 1 + (B_x^+ + B_x^-)m, \tag{4}$$

where B_X^+ and B_X^- are the contributions from a cation and an anion, respectively. Similarly, $B_X^{+\prime}$ and $B_X^{-\prime}$ were determined by the same method as mentioned above.

The D and ^{17}O nuclei are quadrupole nuclei with spin quantum numbers of I=1 and 5/2, respectively. Under an extreme motional narrowing condition, the relation between R_1 and the reorientational correlation time (τ) is given by

$$R_1 = \frac{3}{40}\frac{2I+3}{I^2(2I-1)}\left(\frac{e^2qQ}{\hbar}\right)^2\left(1+\frac{\eta^2}{3}\right)\tau, \tag{5}$$

where, η is an asymmetric parameter, and $e^2qQ/\hbar$ is a quadrupole coupling constant.

The observed R_1 values represent a fractional ($x^{\pm}$) average of the spin–lattice relaxation rate of bulk D_2O (R_1^0), the cation hydrated D_2O (R_1^+), and the anion hydrated D_2O (R_1^-) molecules. When the exchange of D_2O molecules between a hydrated D_2O bulk D_2O is much faster than nucleus relaxation, the follow equation holds:

$$R_1 = (1 - x^+ - x^-)R_1^0 + x^+R_1^+ + x^-R_1^- \tag{6}$$

Further,

$$x^{\pm} = n^{\pm} \cdot m/50.0, \tag{7}$$

where n^+ and n^- are the coordination numbers of the cation and the anion, respectively. From Eqs. 4, 5, 6, and 7 the following relations are obtained:

$$\frac{R_1}{R_1^0} = 1 + \left\{n^+\left(k^+ \cdot \frac{\tau_x^+}{\tau^0} - 1\right) + n^-\left(k^- \cdot \frac{\tau_x^-}{\tau^0} - 1\right)\right\}\frac{m}{50.0} \tag{8}$$

and

$$k^{\pm} = \{(e^2qQ/\hbar)^{\pm}\}^2/\{(e^2qQ/\hbar)^0\}^2. \tag{9}$$

Here, the k^- value of the D and ^{17}O nuclei is 0.69 for the F^- ion, within experimental error.[8] The k^- values for the Cl^-, Br^-, I^- ions are determined by the following method. Ab initio calculations give the D quadrupole coupling constant as a function of the intramolecular O–D bond length of a D_2O molecule. The relation between the O–H distance and the D coupling constant is given by the following equation:[8]

$$(e^2qQ/\hbar)_D^{\pm} = (e^2qQ/\hbar)_D^0 - p(r_{OH}^{\pm} - r_{OH}^0), \tag{10}$$

Table 1. The B_X, $B_{\bar{X}}$, B'_X, and $B_{\bar{X}}'$ of NMR and B^-[a] of Solution Viscosity at 25°C

Salt	B_X (kg mol^{-1})		B'_X (l mol^{-1})		$B_{\bar{X}}$ (kg mol^{-1})		$B_{\bar{X}}'$ (l mol^{-1})		B^- (l mol^{-1})
	D	^{17}O	D	^{17}O	D	^{17}O	D	^{17}O	
KF	0.088	0.105	0.097	0.116	0.109	0.114	0.120	0.126	0.096[b]
KCl	−0.042	−0.017	−0.046	−0.019	−0.021	−0.009	−0.021	−0.008	−0.02
KBr	−0.067	−0.035	−0.074	−0.039	−0.046	−0.027	−0.051	−0.030	−0.05
KI	−0.087	−0.071	−0.096	−0.078	−0.066	−0.063	−0.073	−0.069	−0.10

a) Ref. 19. b) This is the H_2O value, deteils see text.

where p is 18058 KHz/nm, $r_{OH}^{\pm}$ the intramolecular O–H bond length of a hydrated water, and r_{OH}^{0}=0.098 nm the intramolecular O–H bond length of pure water. The deuterium isotope effect on the O–H bond length has been neglected. The k^+ value of the D nucleus for the K^+ ion, calculated by using Eq. 10 (r_{OH}^{+}=0.097 nm), is 1.14. Under an extrem narrowing condition, there is no different $k^{\pm}$ value for the D and ^{17}O nuclei of a hydrated water molecule.[8] Since Cl^-, Br^-, and I^- ions are structure-breaking ions similar to K^+ ion, we may use 1.14 as the k^-, value of the D and ^{17}O nuclei for the Cl^-, Br^-, I^- ions. In this case, different orientations of water molecules around the anions and cations may be neglected. Finally, from Eqs. 4 adn 8 we can obtain

$$B_{\bar{X}}^{\pm}=\left(k^{\pm}\cdot\frac{\tau_X^{\pm}}{\tau_X^0}-1\right)\frac{n_X^{\pm}}{50.0}. \tag{11}$$

Table 1 shows the B_X, $B_{\bar{X}}$, B'_X, and $B_{\bar{X}}'$values of the NMR and B^- values[19] of the solution viscosities in potassium halides–D_2O systems. In these cases we assumed that B^- of the F^- ion of the D_2O system is equal to that of the H_2O system, since the solvent isotrope effect on the $B^{\pm}$ values for positive hydration ions is small.[19] The mol kg^{-1} unit of B_X and $B_X^{\pm}$ and the mol dm^{-3} unit of B'_X and $B_X^{\pm\prime}$ have a linear relation to the $B^{\pm}$ (mol l^{-1} unit) of the solution viscosity. The effect of the structure-making F^- ion on the $B_{^{17}O}^{-}$ value for ^{17}O relaxation is larger than that on B_D^-, and the effect of the structure-breaking Cl^-, Br^-, and I^- ions on the $B_{\bar{X}}$ values is reversed. On the other hand, the effects of the structure-making Li^+ and Na^+ cations and the structure-breaking K^+ and Cs^+ cations on B_D^+ are larger than those of $B_{^{17}O}^{+}$.[10] The relation between $B_{\bar{X}}'$ and B^- in the D_2O system is of the order of $B_{\bar{X}}' \geqq B^-$. These results regarding the D_2O system are in contrast with the relation $B_H^- < B^-$ in the H_2O system reported by Hertz et al.[1] The reason is due to a different relaxation mechanism between the ^1H nucleus and the D and ^{17}O nuclei. Although the ^1H nucleus is relaxed by dipole–dipole (intra and intermolecular) interactions, the D and ^{17}O nuclei are relaxed by the quadrupole (intramolecular) interaction. Our experimental condition below 1.0 mol kg^{-1} was different from that for the concentration above 1.0 mol kg^{-1} studied by Hertz et al. The relation

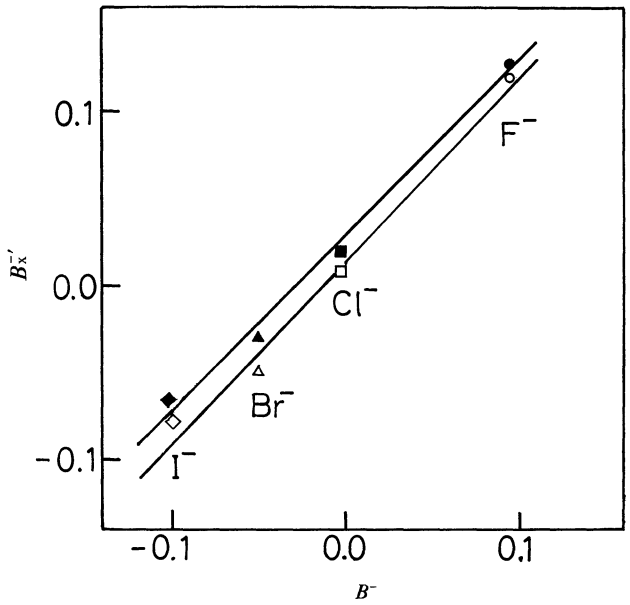

Fig. 3. The relation between $B_{\bar{X}}'$ of NMR method and B^- of solution viscosity at 25°C. The open and closed symboles are X=D and ^{17}O, respectively. The open symbols for different anions are ○: F^-, □: Cl^-, △: Br^-, ◇: I^-.

between $B_{\bar{X}}'$ from the NMR method and B^- from the solution viscosity of halide anions is shown in Fig. 3. The observed linear correlations between $B_X^{\pm\prime}$ and $B^{\pm}$ (mol l^{-1} unit) are given by the following equations:

$$B_D^{-\prime}=1.0B^- + 0.012 \tag{12a}$$

and

$$B_{^{17}O}^{-\prime}=1.0B^- + 0.024 \tag{12b}$$

for anions; for cations[10] it is given by

$$B_D^{-\prime}=0.75B^- + 0.0022 \tag{12a}$$

and

$$B_{^{17}O}^{-\prime}=0.61B^- + 0.0046 \tag{12b}$$

The agreement between the $B_X^{\pm\prime}$ values of NMR (reori-

Table 2. The Limiting Values of a Hydrated D_2O Molecules in Halides Ions at 25°C

Ion	$(R_1)^{-}_{D}/(R_1)^{0}_{D}$	$(R_1)^{-}_{^{17}O}/(R_1)^{0}_{^{17}O}$	$(R_1)^{-}_{D}$ s^{-1}	$(R_1)^{-}_{^{17}O}$ s^{-1}	τ^{-}_{D} ps	$\tau^{-}_{^{17}O}$ ps	$\tau^{-}_{D}/\tau^{-}_{^{17}O}$
F^-	1.91	1.96	4.34	344	6.47	6.64	0.97
Cl^-	0.819	0.908	1.86	160	1.70	1.89	0.90
Br^-	0.638	0.733	1.45	129	1.33	1.51	0.88
I^-	0.433	0.534	0.983	94.0	0.900	1.10	0.82
Pure water			2.27	176	2.38	2.37	1.00

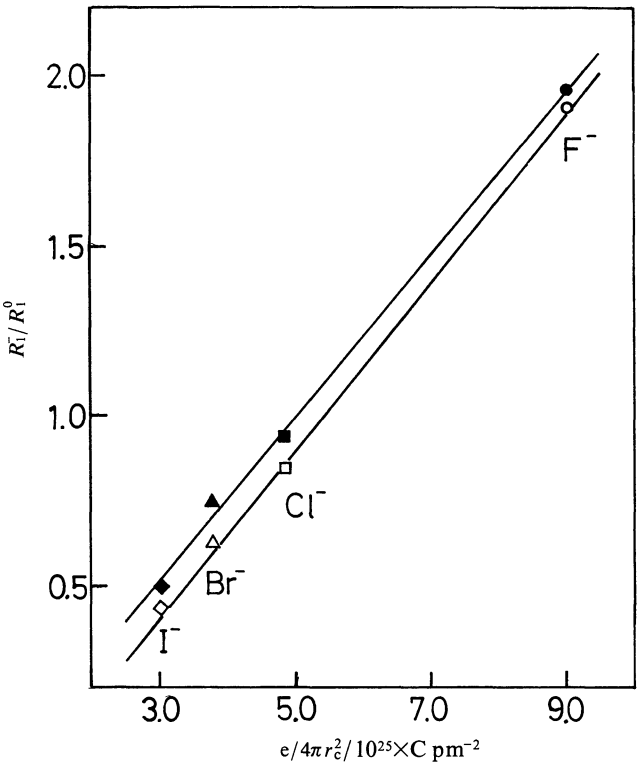

Fig. 4. The relation between the relative relaxation rates (R_1^-/R_1^0) and the surface charge density of ions. The open and closed symbols are X=D and ^{17}O, respectively. The open symbols employed for different anions are ○: F^-, □: Cl^-, △: Br^-, ◇: I^-.

entational motion) and the B^- values for the solution viscosity of anions is somewhat better than those for the cations.

Reorientational Motion of a Hydrated D_2O Molecule. Van der Maarel et al. estimated the relaxation of both the D and ^{17}O nuclei of the hydrated water molecules of cations in the limit of infinite dilution by using a polynominal relation between R_1/R_1^0 and the salt concentration. Both reorientational correlation times of the D and ^{17}O nuclei of hydrated water molecules of an hydration sphere are equal within the experimental error, as in the case of pure D_2O molecules, i.e., isotropic reorientational motion. On the other hand, the relaxation rate of the D nucleus of hydrated water molecules is smaller than that of the ^{17}O nucleus in the high-concentration range above 1.0 mol kg^{-1}, i.e., anisotropic reorientational motion. From this result at high concentration, they expected anisotropic reorientational motion of hydrated water molecules at infinite dilution. Especially for the F^- ion, being the largest surface-charge density among univalent anions, a significant ion–water interaction was suggested from several experimental results.

Table 2 shows the corrected $(R_1)^{-}_{X}/(R_1)^{0}_{X}$, $(R_1)^{-}_{X}$, τ^{-}_{X}, and $\tau^{-}_{D}/\tau^{-}_{^{17}O}$ values at infinite dilution. They were determined from the linear relation between $(R_1)^{-}_{X}/(R_1)^{0}$ given by Eqs 8—11 and the surface charge density of ions, as shown in Fig. 4. As shown in Table 2, although the reorientational motion of a hydrated D_2O molecule in Cl^-, Br^-, and I^- ions (negative hydration anions) is anisotropic, the reorientational motion of a hydrated D_2O molecule in F^- ions is approximetly isotropic. From these results, it is clear that the anisotropy of reorientational motion of an anionic hydrated D_2O molecule is enhanced with increasing anionic radius.

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