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NMR Studies on Reorientational Motion of Hydrated D_2O Molecules in Tetraalkylammonium Bromide Dilute Aqueous Solutions

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The spin-lattice relaxation times of D and ^{17}O nuclei of hydrated D_2O molecules in tetraalkylammonium bromide (Me_4NBr, Et_4NBr, Pr_4NBr, and Bu_4NBr) dilute aqueous solutions in the concentration range of 0.2 to 1.0 mol kg^{-1} at 25 °C were measured by NMR spectroscopy. The relaxation rates of D and ^{17}O nuclei varied linearly with increasing the concentration below 1.0 mol kg^{-1}. The dynamic hydration number, B_X^+, is defined by $B_X^+=(k\cdot\tau_X^+/\tau_X^0-1)n_X^+/50.0$, where τ_X^+ and τ_X^0 (X=D or ^{17}O) are the reorientational correlation times of hydrated D_2O molecules (n_X^+) in R_4N^+ (R: alkyl group) and pure D_2O molecule. The B_X^+ increases with increasing the alkyl chain length of R_4N^+ ions. The abnormally large B_X^+ values, compared with those of alkali metal ions, are caused by the hydrophobic hydration around the alkyl group of the R_4N^+ ion. The reorientational motion of a hydrated D_2O molecule in the hydration sphere of R_4N^+ ions is isotropic, though the motion of a D_2O molecule in the ionic hydration of alkali metal ions is anisotropic.

Symmetrical tetraalkylammonium salts are interesting 1:1 electrolytes whose properties include a tetrahedral simple sphere of cations, the availability of a series of cations with different alkyl chain lengths, and high solubilities in water. The salts are also hydrated in aqueous solution and form clathrate hydrates. Such interesting molecular and physical properities of these salts in water have attracted much attention of physical chemists.[1] Frank and Evans[2] proposed a theory of iceberg formation around the hydrocarbon groups of these ions in water, i.e., hydrophobic hydration. A detail X-ray structure analysis of the clathrate hydrates[3] is useful to understand the different thermodynamic properties of the tetraalkylammonium salts from the inorganic electrolyte solutions from the viewpoint of hydrophobic hydration.

From a study of the concentration dependence on the apparent molal volumes of salts in dilute solution up to 1 M (1 M=1 mol dm^{-3}), the molal volume deriates from the Debye–Hückel limiting slope with increasing concentration.[4,5] For Me_4NBr the slope is slightly positive and becomes more negative upon increasing the alkyl chain length of the tetraalkylammonium salts from Et_4NBr to Bu_4NBr. This is explained by a balancing of two opposite effects: the hydrophobic effect of the alkyl groups and the charge effect of ions. The charge effect trends to increase the apparent molal volume against the square root of the concentration, while the hydrophobic effect decreases it. Water molecules in the vicinity of the Me_4N^+ ion are predominantly influenced by the charge effect, which is weakened for the Et_4N^+ ion and becomes negligible for the Bu_4N^+ ion. A number of data regarding the partial molal volume[6—8] and apparent molal adiabatic compressibilities[9,10] suggest that the structure-making effect of tetraalkylammonium ions is enhanced upon increasing the carbon number of the alkyl groups. Furthermore, Key et al.[11,12] have made a systematic investigation of the viscosities and conductances of tetraalkylammonium salt solutions and have determined the *B* coefficients and the limiting Walden products from them. Pr_4N^+ and Bu_4N^+ ions form a hydrogen-bonding network structure among water molecules in their vicinity, and behave as structure-making ions. The Me_4N^+ ion has a structure-breaking properties and the Et_4N^+ ion has a mixed behavior regarding structure-making and structure-breaking effects.

The dynamic aspect of D_2O molecules of R_4NBr solutions up to 6 mol kg^{-1} was studied by Hertz et al.[13] using the NMR method. They observed that the reorientation time of D_2O molecules becomes longer upon passing from Me_4N^+ to Pr_4N^+ ions. It has been clarified that the reorientational time of a D_2O molecule in a Pr_4NBr solution is longer than that in a Bu_4NBr solution at high salt concentrations above 1.0 mol kg^{-1}. This conclusion is inconsistent with those derived from thermodynamic and transport properties. This discrepancy may be due to the determination of the reorientation time of infinitly isolated complexes from the extrapolation of high salt concentrations. It is thus necessary to undertake precise NMR measurements of D_2O molecules in a tetraalkylammonium salt dilute solution below 1 mol kg^{-1}.

In the present study we focused on the dynamic properties of the hydrophobic hydration in R_4NBr (R=Me, Et, Pr, and Bu) aqueous solutions are measured the concentration dependence of D and ^{17}O spin-lattice relaxation 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, and the difference between the hydrophobic hydration of tetraalkylammonium ions as well as the hydration of alkali metal ions.

Experimental

Samples. R_4NBr (R=Me, Et, Pr, and Bu) salts from Nakarai Tesque, Inc. (extra pure grade) were recrystallized from water or ethanol. D_2O was obtained from CEA, containing over 99.8% (*d*). Sample solutions were passed through membrane filters with a pore size 0.1 μm to remove dust. Sample solutions were bubbled with nitrogen gas for about five minutes just before NMR measurements to remove any oxygen gas.

NMR Measurement. All D and ^{17}O relaxation times were obtained on a JEOL GX-270 pulsed spectrometer operating at 41.5 and 36.6 MHz, respepctively. Samples were kept in a 10 mm diameter glass tube. The resolution was established by the D nucleus of neat D_2O before the sample measurement. The spin-lattice relaxation times (T_1) were measured by the inversion-recovery method, 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 spectral widths were 1200 Hz for the D nucleus and 60000 Hz for the ^{17}O nucleus. The free induction decay of the D and ^{17}O nuclei were accumulated 4 to 16 times and 100 to 3200 times, respectively, depending on the concentration. Their productibility of the T_1 measurements was within 2%. The temperature was controlled to 25±0.1 °C by an air compressor.

Results and Discussion

Figures 1 and 2 show the concentration dependence of R_1/R_1^0 of D and ^{17}O nuclei of D_2O molecules in R_4NBr with those of alkali metal bromides solutions at 25 °C.

The R_1/R_1^0 values vary linearly with increasing concentration up to 1.0 mol kg^{-1}, similar to those alkali metal bromides.[14] Their positive slopes for D and ^{17}O nuclei are much steepper than those of Li and Na salts, and increase with increasing alkyl chain length of R_4NBr salts. The concentration dependence of R_1 of D and ^{17}O nuclei is given by a linear equation below 1.0 mol kg^{-1}:

$$R_1 = (1 + B_X m)R_1^0, \qquad (X = D \text{ or } {}^{17}O) \qquad (1)$$

where R_1 and R_1^0 are the spin-lattice relaxation rates of the D_2O molecule at a concentration *m* of a R_4NBr solution and pure D_2O, respectively. The $B_X^{\pm}$, of a cation (+) and an anion (−) to B_X is determined by using the following equation and the previous method:[14]

$$R_1 = \{1 + (B_X^+ + B_X^-)m\}R_1^0. \qquad (2)$$

D and ^{17}O nuclei are quadrupole nuclei with spin quantum numbers of I=1 and 5/2, respectively. These nuclei relax mainly be an electric quadrupole interaction. Under the experimental conditions of the motional narrowing limit ($2\pi\nu\tau \ll 1$), where ν is the resonance frequency of this expepriment, the relation between the spin-lattice relaxation rate (R_1) and the rotational correlation time (τ) is given by the following equation:[15]

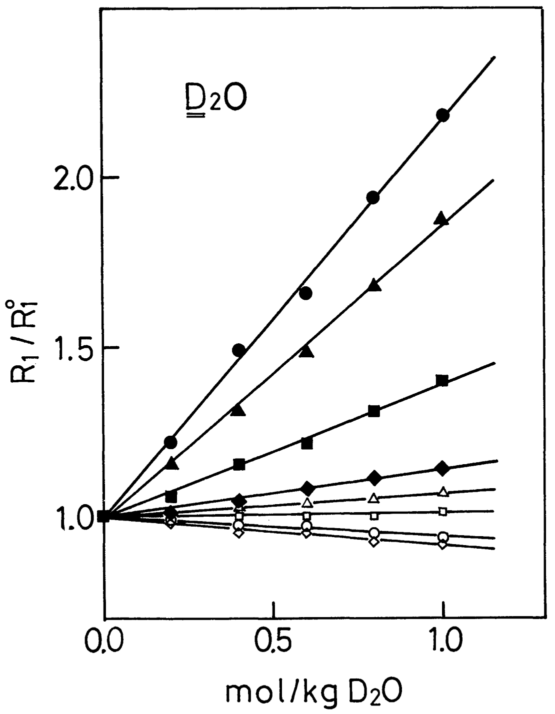

Fig. 1. Plots of D relaxation rates (R_1/R_1^0) of a D_2O molecule in tetraalkylammonium and alkali metal[a)] bromide solutions at 25 °C. ◆: Me_4NBr, ■: Et_4NBr, ▲: Pr_4NBr, ●: Bu_4NBr, △: LiBr, □: NaBr, ○: KBr, ◇: CsBr. a) Ref. 14.

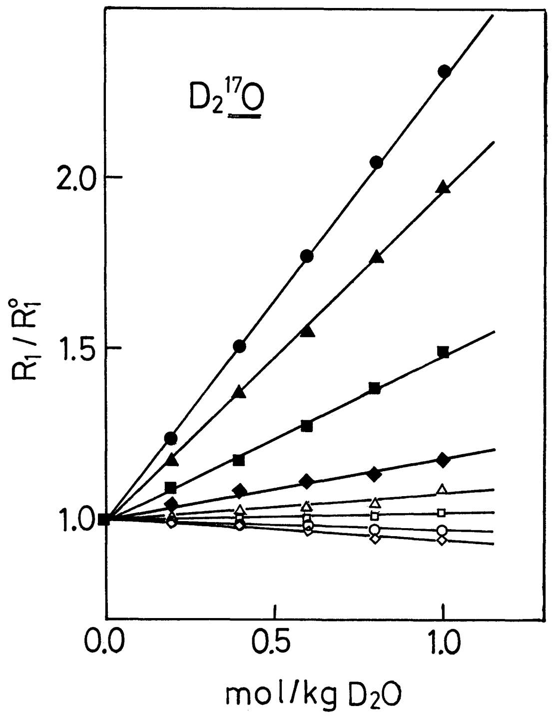

Fig. 2. Plots of ^{17}O relaxation rates (R_1/R_1^0) of a D_2O molecule in tetraalkylammonium and alkali metal[a)] bromide solutions at 25 °C. ◆: Me_4NBr, ■: Et_4NBr, ▲: Pr_4NBr, ●: Bu_4NBr, △: LiBr, □: NaBr, ○: KBr, ◇: CsBr. a) Ref. 14.

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

Here, I, η, and $e^2qQ/\hbar$ are the quantum number, the asymmetry parameter, and the quadrupole coupling constant, respectively. For a pure D_2O molecule $e^2qQ/\hbar=254$ kHz and $\eta=0.135$[16] are for a D nucleus, and $e^2qQ/\hbar=8.1$ MHz and $\eta=0.75$[16] are for an ^{17}O nucleus. For a pure D_2O molecule τ_D^0 and $\tau_{^{17}O}^0$ are 2.38 ps and 2.37 ps.

Since R_1 increases linearly with increasing concentration for all R_4NBr salts, it is reasonable that R_1 is the fractional average of the spin-lattice relaxation rates of bulk D_2O (R_1^0), an anion hydrated D_2O (R_1^-) and a cation hydrated (R_1^+) D_2O molecule given by the following equations:

$$R_1 = (1 - x^+ - x^-)R_1^0 + x^-R_1^- + x^+R_1^+ \tag{4}$$

and

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

where R_1^0, R_1^+, R_1^-, n^+, and n^- are the spin-lattice relaxation rates of pure water, hydrated water of the cation and anion, and the hydration numbers of the cation and anion, respectively.

From Eqs. 3 and 4, the following relations are obtained:

$$\frac{R_1}{R_1^0} = 1 + \{n^+(k^+\cdot\frac{\tau_X^+}{\tau^0} - 1) + n^-(k^-\cdot\frac{\tau_X^-}{\tau^0} - 1)\}\frac{m}{50.0} \tag{5}$$

and

$$k^{\pm} = \{(e^2qQ/\hbar)^{\pm}/(e^2qQ/\hbar)^0\}^2, \tag{6}$$

where τ^0, τ_X^+, and τ_X^-, are the reorientation time of pure D_2O, and D_2O in the hydration sphere of a cation and an anion, respectively. Here, $k=1$ in the case of $(e^2qQ/\hbar)^+=(e^2qQ/\hbar)^0$ and $k=0.82$[17] in the case of $(e^2qQ/\hbar)^+=(e^2qQ/\hbar)^{Li^+ \text{ or } Na^+}$. Finally, from Eqs. 2 and 5, we can obtaine the following relation between $B_X^{\pm}$ and $\tau_X^{\pm}$:

$$B_X^{\pm} = (k^{\pm}\cdot\frac{\tau_X^{\pm}}{\tau_X^0} - 1)\frac{n_X^{\pm}}{50.0}. \tag{7}$$

$B_X^{\pm}$ is related to the reorientation time, $\tau_X^{\pm}$, and was defined as the dynamic hydration number by Uedaira et al.[18,19]

$B_X^{\pm}$, $\tau_X^{\pm}/\tau_0$ and $\tau_D^{\pm}/\tau_{^{17}O}^{\pm}$ are shown in Table 1. The B_X^+ values for D and ^{17}O nuclei are of the order of

$(Cs^+<K^+<0<Na^+<Li^+)$[14]$<Me_4N^+<Et_4N^+<Pr_4N^+<Bu_4N^+$.

The relaxation rates of D and ^{17}O nuclei of D_2O molecules over the whole concentration range of R_4NBr solutions increase with increasing alkyl chain length of the R_4N^+ ion. These results are in contrast with those of Hertz et al.[13] Further, Hertz et al. reported that the self-diffusion coefficients[20] of Bu_4N^+ and Pr_4N^+ ions show the same behavior as R_1.[13] Our results are reasonable for those of the thermodynamic and transport properties, which change as a linear function of the alkyl chain length of R_4NBr. We consider these differences between our experimental results and Hertz et al.[13] Our experiments were carried out at a lower concentration range, below 1.0 mol kg^{-1}, than those above 1.0 mol kg^{-1} studied by Hertz et al.[13] Above 1.0 mol kg^{-1} the curious behavior of the physical properties of the Bu_4N^+ ion against the concentration has been reported. For example, the apparent molar volume of a Bu_4NBr solution shows a minima at about 1.0 M, and above 1.0 M makes a micell.[4,21,22]

The dynamic hydration number as a function of the ionic crystal radius (r_c) is shown in Fig. 3. The curves of B_D^+ and $B_{^{17}O}^+$ vs. r_c plots for both D and ^{17}O nuclei pass through minima at 200—250 pm. Alkali metal ions show a negative slope and R_4N^+ ions have a positive one. The dependence of r_c on B_X^+ for the R_4N^+ ion is larger than those of alkali metal ions. This tendency corresponds to the B coefficient of the solution viscosity vs. r_c plots. The absolute values of four R_4N^+ ions are larger than those of alkali metal ions. Since the Li^+ ion has the smallest ionic radii among univalent cations and has the largest surface charge density, it is natural that hydrated D_2O molecules of Li^+ ion are strongly electrostricted around the Li^+ ion through a ion-water interaction and that the reorientational motion is mostly repressed among the alkali metal ions. Even if the surface charge density of the R_4N^+ ion is smaller than that of alkali metal ions, the large B_X^+ values of hydrated D_2O molecules of R_4N^+ ions are considered for the following reasons. One is due to the large number of

Table 1. Hydration Behaviors of Tetraalkylammonium Ion in Aqueous Solution at 25 °C

	B_D^+	$B_{^{17}O}^+$	n^+ [a]	τ_D^+/τ_D^0 [b]	$\tau_{^{17}O}^+/\tau_{^{17}O}^0$ [b]	τ_D^+/τ_D^0 [c]	$\tau_{^{17}O}^+/\tau_{^{17}O}^0$ [c]	$\tau_D^+/\tau_{^{17}O}^+$
Me_4N^+	0.177	0.200	25	1.35	1.40	1.65	1.71	0.96
Et_4N^+	0.432	0.498	30	1.72	1.83	2.10	2.23	0.93
Pr_4N^+	0.894	0.970	35	2.28	2.39	2.78	2.91	0.95
Bu_4N^+	1.22	1.32	40	2.52	2.65	3.08	3.24	0.95

a) Ref. 20. b) $k=1$. c) $k=0.82$.

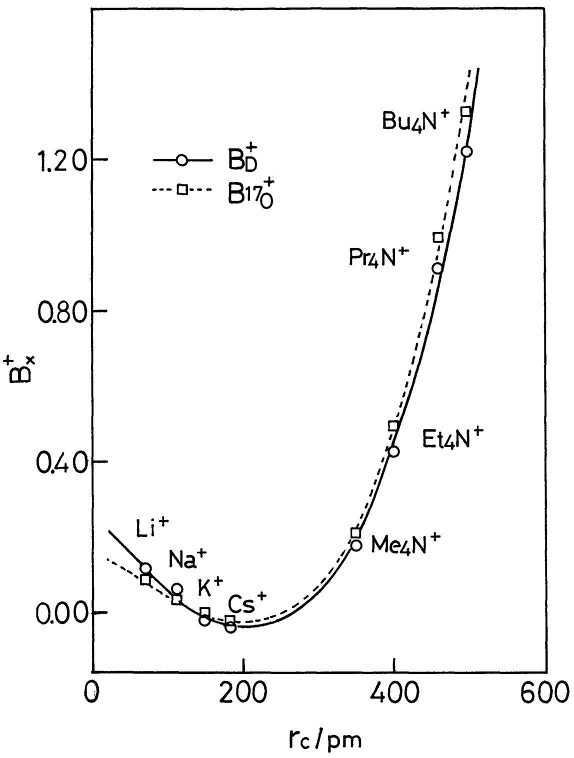

Fig. 3. Plots of the dynamic hydration number in R_4N^+ and alkali metal[a)] ions as a function of their ionic radii. a) Ref. 14.

hydrated D_2O molecules of R_4N^+ ions with increasing alkyl chain length, i.e., ionic radii. The other is hydrophobic hydration around the alkyl chain of R_4N^+ ions, like the clathrate hydrate. These hydrated D_2O molecules are stabilized by the formation of a network structure through hydrogen bonding among D_2O molecules in the hydration sphere. The relative reorientation time of an individual hydrated D_2O molecule, τ_X^+/τ_X^0, is determined by using Eq 6 and known n^+ values. As shown in Table 1, it is clear that both the reorientation times of D and ^{17}O nuclei of a hydrated D_2O molecule for Me_4N^+ or Et_4N^+ ions are shorter than those of the Li^+ ion ($\tau_D^+/\tau_D^0=1.98$, $\tau_{^{17}O}^+/\tau_{^{17}O}^0=1.78$ for $k=1$, and $\tau_D^+/\tau_D^0=2.41$, $\tau_{^{17}O}^+/\tau_{^{17}O}^0=2.17$ for $k=0.82$), but that the reorientation times of a hydrated D_2O molecule for Pr_4N^+ and Bu_4N^+ ions are longer than those of the Li^+ ion. Therefore, the larger B_X^+ values of Me_4N^+ or Et_4N^+ ions than that of the Li^+ ion are due to the large number of hydrated Me_4N^+ and Et_4N^+ ions. On the other hand, the reorientation time of a hydrated D_2O molecule of Pr_4N^+ and Bu_4N^+ ions is essentialy longer than that of an electrostrictly hydrated D_2O molecule of the Li^+ ion. Since R_4N^+ ions have a smaller surface change density than does the Li^+ ion, these large B_X^+ and τ_X^+/τ_X^0 values effectively strengthen D_2O–D_2O interactions.

Struis et al. determined the reorientation times of X nuclei, τ_X (X=D and ^{17}O), in pure water as a function of the temperature over the range of −10 to 53 °C.[16)] The ratio of the reorientation times of a water molecule at a certain temperature, τ_X^t, to the reorientation time at 25 °C, τ_X^{25}, (the relative reorientational time τ_X^t/τ_X^{25}) increases with decreasing temperature. Comparing the reorientation times of hydrated water molecules of R_4N^+ ions with those of water molecules in bulk water at various temperatures, the reorientation times of Me_4N^+, Et_4N^+, Pr_4N^+, and Bu_4N^+ ions correspond to those of a water molecule at 14, 7, 0, −2 °C, for $k=1$, and 9, 3, −4, −7 °C for $k=0.82$, respectively. Especially, it is interesting that the reorientational motion of a hydrated water molecule of Pr_4N^+ and Bu_4N^+ ions corresponds to the motion of a pure water molecule below 0 °C.

The reorientational motion of a quadrupole nuclei is related to the reorientational motion of the main component of the quadrupole interaction tensor. The main component of the ^{17}O nucleus in a D_2O molecule lies along the perpendicular axis to the molecular plane and the D nucleus is almost along the O–D bond axis. From this point of view, we can estimate the anisotropic reorientational motion ($\tau_D^+/\tau_{^{17}O}^+$) of a hydrated D_2O molecule in the hydration sphere. The $\tau_D^+/\tau_{^{17}O}^+$ is 0.96, 0.93, 0.95, and 0.95, for Me_4N^+, Et_4N^+, Pr_4N^+, and Bu_4N^+ ions, respectively, as shown in Table 1. These results tell us that the reorientational motion of a hydrated D_2O molecule in R_4N^+ ions is isotropic within experimental uncertainty, in spite of the fact that τ_X^+/τ_X^0 increases largely with increasing alkyl chain length.

In a previous report we reported that the anisotropy of the reorientational motion ($\tau_D^+/\tau_{^{17}O}^+$) of hydrated water molecules in alkali metal ions is 1.12 and 1.13 for the positive hydration of Li^+ and Na^+ ions, and 0.89 and 0.92 for the negative hydration of K^+ and Cs^+ ions, respectively. The $\tau_D^+/\tau_{^{17}O}^+$ values of a hydrated water molecule of R_4N^+ ions exist between positive and negative hydration ions. The reorientational motion of pure water molecules is almost isotropic at temperatures between −10 °C and 53 °C.[16)] The dynamic structure of the hydrophobic hydration in R_4N^+ ions is like that of pure water, since the reorientational motion is slow and isotropic.

Finally, from both present and previous studies it has been clarified that there are three kinds of the dynamic hydration numbers: the positive hydration of Li^+ and Na^+ is $0<B_{^{17}O}^+<B_D^+$, the negative hydration of K^+ and Cs^+ is $B_D^+<B_{^{17}O}^+<0$, and the hydrophobic hydration of R_4N^+ is $0\ll B_{^{17}O}^+=B_D^+$. The reorientation motion of a D_2O molecules in the hydrophobic hydration of R_4N^+ ions is isotropic though anisotropic motion of the D_2O molecule in the ionic hydration of alkali metal ions.

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