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An Evaluation of the Overall Rotational Correlation Times of Tetraalkylammonium Ions in Solution.
^{13}C NMR Relaxation Study

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The ^{13}C NMR spin-lattice and spin–spin relaxation times (T_1 and T_2), and the nuclear Overhauser effect (NOE) were measured for tetraalkylammonium ions (R_4N^+, $R = C_2H_5$ (Et), n-C_3H_7 (n-Pr), n-C_4H_9 (n-Bu), and n-C_5H_{11} (n-Pen)) in the concentrated aqueous solutions of their bromides or chlorides. A minimum was observed in the temperature dependence of T_1 for the α-carbon in each solution. The value was 1.2—1.4 times higher than that predicted assuming only the isotropic overall rotation of the R_4N^+ ion. This increase in the T_1 minimum values was ascribed to the rotations around the N–α-C bonds with an restriction in the azimuthal angle for each bond. The ranges where the N–α-C bonds could rotate with the time scales much less than those for the overall rotations were determined by the values of the T_1 minima for the corresponding R_4N^+ ions as $\pm 20°$, $\pm 17°$, $\pm 20°$, and $\pm 20°$ centering the gauche conformations, respectively, for Et_4N^+, n-Pr_4N^+, n-Bu_4N^+, and n-Pen_4N^+. These values well reproduced the T_2 and NOE values observed at various temperatures in the concentrated aqueous solutions of the R_4N^+ halides. By using the thus obtained ranges of the azimuthal angles, the overall rotational correlation times in the dilute aqueous solutions (0.01 mol kg^{-1}) were also determined. The obtained rotational correlation times were compared with those calculated using the Stokes–Einstein–Debye equation and the effect of the hydrophobic hydration was discussed.

Solutions of symmetrical tetraalkylammonium salts have been a target of a number of studies using various techniques. These studies have contributed to revealing the fundamental problems of electrolyte solution, because of the simple geometrical structure of their cations and the capability of systematic change in the ionic sizes by properly choosing the alkyl groups.[1] The aqueous solutions of these salts are also important as model systems for hydrophobic hydration because of the high solubility in water, in spite of the significant hydrophobic nature of the tetraalkylammonium ions.[1,2]

Ionic translation and rotation are important probes for the dynamic features of solvation. Many studies of the ionic translation (ionic conductance) of R_4N^+ ion have been reported. The results play an important role in characterizing the dynamic and static features of the solvation (hydration) in relation to variation in the ionic size and the hydrophobicity through Walden's rule, based on Stokes' law.[3,4] On the other hand, no quantitative information on the rotational motion of the R_4N^+ ion has been reported.[5] However, a systematic study, e.g., solvent and temperature dependences of the rotational correlation times of various sizes of R_4N^+ ions, is important for the following reasons.

(i) In general, continuum models, such as the hydrodynamic or the dielectric friction model, do not hold or only partially hold for the translational and rotational motions when the size of an ion (molecule) is not sufficiently larger than that of the solvent molecule.[6,7] However, the limitation of applying the continuum models is more lenient for translation than rotation of a spherical ion (molecule); the models can be, at least phenomenologically, applicable to smaller ions in the translation than in the rotation.[8,9] Therefore, the tetraalkylammonium ion with a wide variation in its ionic size is a suitable probe for revealing how the molecularity of a solvent contributes to the ionic translation and rotation and for showing difference in the extent of the contribution of solvent molecularity between ionic translation and rotation.

(ii) The rotational motion of the R_4N^+ ion is also expected to be a good probe for the dynamic features of the hydrophobic hydration, which is proposed to be highly structured with a characteristic hydrogen-bond network, like the clathrate hydrates.[1,2]

The reason why no quantitative rotational correlation time of the R_4N^+ ion in solution has been reported is the lack of a suitable nucleus whose relaxation time directly gives the correlation time of the overall rotation (vide infra); nevertheless, the NMR relaxation measurements are used in a considerable part of the studies dealing with molecular (ionic) rotation.[10] For example, the ^{13}C relaxation of the R_4N^+ ion caused by the magnetic dipolar interaction with the protons is considered to be significantly influenced by the internal rotation around the N–C or C–C bonds, in addition to the overall rotation.[10—12] In such a case, the overall rotational correlation time in solution can not be independently determined without information about the correlation times of the internal rotations based solely on the ^{13}C relaxation measurements, because only a single relaxation time, $T_1 = T_2$, is observed for each nucleus in the alkyl chains under the extreme narrowing condition, i.e., $\tau_c^2\omega^2 \ll 1$, which holds in normal liquid state (τ_c and ω being the correlation time and the NMR resonance frequency).

However, if the time scale of the molecular motion slows down and is comparable or slower than the resonance frequency, i.e., $\tau_c^2\omega^2 \geq 1$, the T_1 and T_2 values show different dependences on the correlation time. Additionally, the NOE value also shows a correlation time dependence.[10,11] In such a case, both of the correlation times (the overall and internal rotations) are thus expected to be independently determined by the measurements of T_1, T_2, and NOE under a given set of conditions, e.g., temperature, pressure, and concentration.

Such sufficient slowing in the rotational motion is realized by using a highly viscous solution. The high solubility of the tetraalkylammonium salts in water allows us to prepare highly viscous concentrated aqueous solutions. Furthermore, the solutions are often easily supercooled.[13—15] For example, the aqueous solution of tetrapropylammonium chloride shows a stable liquid phase even at 200 K in the concentration range of 4.4—5.6 mol kg^{-1}.[13] Under such high concentration and low temperature, the time scale of the overall rotation of R_4N^+ is expected to be comparable to or slower than that of the NMR resonance frequency (ca. 10^{-9} rad s^{-1}). The ^{13}C T_1 and T_2 as well as the NOE measurements for the concentrated aqueous solution of the tetraalkylammonium salts will thus make it possible to determine experimentally the correlation times of the overall rotation and the internal motion of the alkyl chains.

In this paper, we present an attempt to determine the overall rotational correlation times of a series of the R_4N^+ ions ($R = C_2H_5$ (Et), n-C_3H_7 (n-Pr), n-C_4H_9 (n-Bu), and n-C_5H_{11} (n-Pen)) from the observed ^{13}C-T_1, T_2, and NOE values in the concentrated aqueous solutions of the chlorides or bromides at various temperatures. This method is also extended to the dilute solutions.

Experimental

The ^{13}C NMR spectra were measured with a JEOL GX270 FT-NMR operated at 64 MHz (6.7 T) using 5 mm (o.d.) Pyrex tubes. The measurements for the dilute solutions of the tetraalkylammonium salts (below 0.3 mol kg^{-1}) were carried out using a JEOL GSX 400 FT-NMR operated at 100 MHz (9.4 T) using 10 mm (o.d.) tubes. The T_1 and T_2 measurements were carried out using the inversion recovery and the Carr–Purcell, Meiboom–Gill method, respectively, under proton decoupling. For each sample solution, the measurements were repeated several times at a few representative temperatures; consistent results (within 5% for T_1 and 10% for T_2) were obtained. The factors for the nuclear Overhauser enhancement ($\chi_{\rm NOE}$) were determined using a gating decoupling method. The experiments were set up to take three or more sets of peak areas with and without NOE. The estimated error in $\chi_{\rm NOE}$ was ± 0.1 or less. The NMR-probe temperature was controlled within $\pm 0.5\,^\circ$C with a JEOL GVT2 temperature control unit. Since the temperature increase in the sample solutions due to proton irradiation depends on the salt concentration, the temperatures of the sample solutions during the ^{13}C NMR measurements were determined as follows. Temperatures were measured for the solutions with different salt concentrations by placing a thermocouple in the solutions at the position of the rf coil center under the same proton-decoupling conditions as in the measurements of T_1, T_2 or NOE. The concentration dependence of the temperature increase was thus calibrated prior to the ^{13}C NMR measurements. The proton decoupling power was adjusted as low as possible to minimize temperature increase of the solutions.

Et_4NCl, n-Pr_4NBr, n-Bu_4NCl, and n-Pen_4NCl were purchased from Wako Chemicals Co., Ltd. The tetraalkylammonium salts were dissolved in distilled water after twice-repeated recrystallizations from an ethanol–ether mixture and then were dried in a vacuum. The sample solutions were degassed by the usual freeze-thaw cycle and were shielded under vacuum.

For the concentrated solutions, in order to make the overall rotation sufficiently slower than the time scale of the resonance frequency, the concentrations of the R_4N^+ salts and the counter ion were chosen so as to give stable solution phases at a temperature as low as possible, referring to the results of the DTA or DSC measurements as shown in Table 1.[13,14,16]

The molecular mechanics calculations were performed with the MM2 force field mounted on the Chem3D program (Cambridge Scientific Computing, Inc. Ver. 3.1.2). The MM2 parameters given in the program were used without any modification.

Results and Discussion

Temperature Dependence of the ^{13}C NMR in the Concentrated Aqueous Solutions of the Tetraalkylammonium Salts. When the relaxation of a ^{13}C nucleus is caused by the magnetic dipole–dipole interaction with the protons directly attached to the carbon atom, the ^{13}C–T_1, T_2, and $\chi_{\rm NOE}$ are represented by:[17]

$$T_1^{-1} = (1/10)K_{\rm m}[J(\omega_1) + 3J(\omega_3) + 6J(\omega_4)], \tag{1a}$$

$$T_2^{-1} = (1/20)K_{\rm m}[4J(0) + J(\omega_1) + 6J(\omega_2) + 3J(\omega_3) + 6J(\omega_4)], \tag{1b}$$

$$\chi_{\rm NOE} = \left(\frac{\gamma_{\rm H}}{\gamma_{\rm C}}\right) \times \frac{[6J(\omega_4) - J(\omega_1)]}{[J(\omega_1) + 3J(\omega_3) + 6J(\omega_4)]}, \tag{1c}$$

and

$$\omega_1 = \omega_{\rm H} - \omega_{\rm C}, \quad \omega_2 = \omega_{\rm H}, \quad \omega_3 = \omega_{\rm C}, \quad \omega_4 = \omega_{\rm H} + \omega_{\rm C}, \tag{2a}$$

Table 1. The Glass Forming Temperatures, $T_{\rm g}$, and the Critical Temperatures for the Overall Rotational Correlation Times, T_0, for the Aqueous Solutions of Various Tetraalkylammonium Salts

Compound	m/mol kg^{-1}		$T_{\rm g}$/K		T_0/K[a)]
Et_4NCl	5.6		176[b)]		175
n-Pr_4NBr	6.1			198[c)]	183
	4.3			196[c)]	178
	3.5	(245)[c,d)]	(226)[c,d)]	193[c)]	—
	2.7	(254)[c,e)]			—
	1.4	(256)[c,e)]			—
n-Bu_4NCl	7.9	(259)[c,f)]			—
n-Pen_4NCl	0.26	(261)[c,f)]			—

a) The value was determined by fitting the temperature dependence of $\tau_{\rm r}$ to Eq. 5. (See text). b) The data from Ref. 13. c) Y. Masuda, unpublished data. d) The value corresponds ice forming or crystallization temperature. e) The value corresponds ice forming temperature. f) The value corresponds a temperature of ice forming or crystallization of the clathrate hydrate. (See Ref. 14).

$$K_{\mathrm{m}} = n\gamma_{\mathrm{C}}^2\gamma_{\mathrm{H}}^2\hbar^2 r_{\mathrm{CH}}^{-6}, \tag{2b}$$

where γ_{C}, γ_{H}, ω_{C}, and ω_{H} represent the gyromagnetic ratios and the resonance frequencies of ^{13}C and ^{1}H, respectively. n and r_{CH} indicate the number of the protons attached to the ^{13}C atom and the C–H bond length, respectively, and the latter is taken to be 0.111 nm. When only an isotropic overall rotation is responsible for the ^{13}C relaxation, the spectral density of the dipolar-field fluctuation, $J(\omega_i)$, is represented by:

$$J(\omega_i) = \frac{\tau_{\mathrm{c}}}{1+\omega_i^2\tau_{\mathrm{c}}^2}, \tag{3}$$

where τ_{c} indicates the correlation time responsible for the magnetic relaxation, i.e., the overall rotational correlation time in this case.

The temperature dependences of the ^{13}C–T_1, T_2, and χ_{NOE} values for the α- and β-carbons of $\mathrm{R_4N^+}$ (R=Et, n-Pr, n-Bu, and n-Pen) in the concentrated aqueous solutions of the salts are shown in Figs. 1, 2, and 3. Above room temperature, the observed χ_{NOE} values were equal to 1.98 within the experimental error, except for 7.9 mol kg^{-1} n-$\mathrm{Bu_4NCl}$ and 0.26 mol kg^{-1} n-$\mathrm{Pen_4NCl}$ solutions.[18] These results indicate that the ^{13}C relaxations are totally caused by the magnetic dipolar interaction with the attached protons and that the time scale of the correlation times, τ_{c}, is fast enough to satisfy the extreme narrowing limit, i.e., $\tau_{\mathrm{c}}^2\omega^2 \ll 1$.[17] In the present study, the magnetic dipolar interactions are assumed to be only the causes of the α- and β-^{13}C relaxations of all the $\mathrm{R_4N^+}$ ions.[18]

For both the α- and β-^{13}C nuclei in all the $\mathrm{R_4N^+}$ ions, each temperature dependence of T_1 showed a minimum at a certain temperature, and a drop in the χ_{NOE} value was observed at that temperature, while the T_2 value monotonously decreases with decrease of temperature. The temperatures showing the T_1 minima (and the χ_{NOE} drops) for the α- and β-carbons were almost the same for each solution of the $\mathrm{R_4N^+}$ salts, indicating the existence of a common dynamics responsible for the relaxations of the α- and β-carbons, such as the overall rotation of the $\mathrm{R_4N^+}$ ion.

Thus, it seems that the overall rotations of the $\mathrm{R_4N^+}$ ions are the predominant dynamics for determining the features of the obtained temperature dependences of T_1, T_2, and χ_{NOE} of the α- and β-carbons. However, the obtained values of the T_1 minima were significantly higher than those predicted by Eqs. 1a, 2, and 3, where only an isotropic (overall) rotation is assumed (See Figs. 1, 2, and 3). This result indicates that dynamic modes other than the overall rotation also contribute to the magnetic relaxations, and that the correlation times of the dynamics are much faster than the overall rotation.[17] These faster modes are assigned to the internal rotations around the N–α-C and α-C–β-C bonds in the alkyl chains.

A Model for Analyzing the NMR Data. Considering the above features of the observed temperature dependences of T_1, T_2, and χ_{NOE}, we made the following quantitative analysis assuming the overall rotation of the $\mathrm{R_4N^+}$ ion and the internal rotations around the N–C or C–C bonds, including the additional restrictions for the internal motions based on the X-ray structure of the clathrate hydrates[19—21] and the results of the strain energy calculations for the conformational changes of the alkyl chains.

The X-ray structures of the clathrate hydrates, e.g., (n-$\mathrm{Bu_4N}$)($\mathrm{C_6H_5COO}$)·39.5$\mathrm{H_2O}$, show that the conformations around the all C–C bonds are trans.[20,21] Slight disorders are, however, found in the positions of the α- and β-carbons, while the dihedral angles around the β-C–γ-C and γ-C–$\mathrm{CH_3}$ bonds show large disorder. These results indicate considerable restrictions for large amplitude rotations around the N–α-C and α-C–β-C bonds, such as the gauche to gauche or the *trans* to *gauche* conformational change. The extent of the restrictions for the rotations around the N–α-C and the α-C–β-C bonds was confirmed by a molecular mechanics calculation. Figure 5 shows the results of the calculation for the total strain energies at the various azimuthal angles, ϕ, as defined in Fig. 4, for the N–α-C and the α-C–β-C bond of an isolated n-$\mathrm{Pr_4N^+}$ ion.[22] The calculated strain energies showed only a slight dependence of the azimuthal angle within $\phi = \pm 16°$ and $\pm 20°$, respectively, for the N–α-C and α-C–β-C bonds. These energies steeply increased beyond these angles. This result leads to the following dynamic feature for the alkyl chains; i.e., the rotations around the N–α-C or α-C–β-C bonds are almost free within boundary angles $\pm\theta$, and a large amplitude rotation, i.e., the trans to gauche conformational change in the alkyl chains, seldom happens.[23]

Considering the previously mentioned situation, we assume the following model to analyze the observed T_1, T_2, and χ_{NOE} values for the α- and β-carbons in the $\mathrm{R_4N^+}$ ions.

(i) The rotation around each N–α-C and α-C–β-C bond is restricted within a boundary angle $\pm\theta$, i.e., the correlation time of the rotation beyond the angle is much larger than that for the overall rotation.[23]

(ii) The internal rotation within the angle, $\pm\theta$, is much faster than the overall rotation of the $\mathrm{R_4N^+}$ ion and the inverse of ω_i in Eq. 2a.

Under such conditions, $J(\omega_i)$ for the α-carbon in Eqs. 1a, 1b, and 1c is given by London et al., that is,[24]

$$\begin{aligned} J(\omega_i) &= a \times \frac{\tau_{\mathrm{r}}}{1+\omega_i^2\tau_{\mathrm{r}}^2} \\ &= \left[\left(\frac{3\cos^2\varphi - 1}{2}\right)^2 + 3\sin^2\varphi\cos^2\varphi\left(\frac{\sin\theta}{\theta}\right)^2 \right. \\ &\quad \left. + \frac{3}{4}\sin^4\varphi\left(\frac{\sin 2\theta}{2\theta}\right)^2\right] \times \frac{\tau_{\mathrm{r}}}{1+\omega_i^2\tau_{\mathrm{r}}^2}, \end{aligned} \tag{4}$$

where τ_{r} and φ respectively represent the correlation time of the overall rotation and the angle between the N–α-C and α-C–H bonds and φ is taken to be 109°.

Evaluation of the Overall Rotational Correlation Times. The restricted angle, θ, for the rotation around the N–α-C bond was determined by the minimum value of the observed temperature dependence of T_1 in each solution, since the minimum value depended only on the angle, as shown in Eq. 4. These results are summarized in Table 2. The obtained θ values ranged between 16—20 degrees. These values are close to the angle where the strain

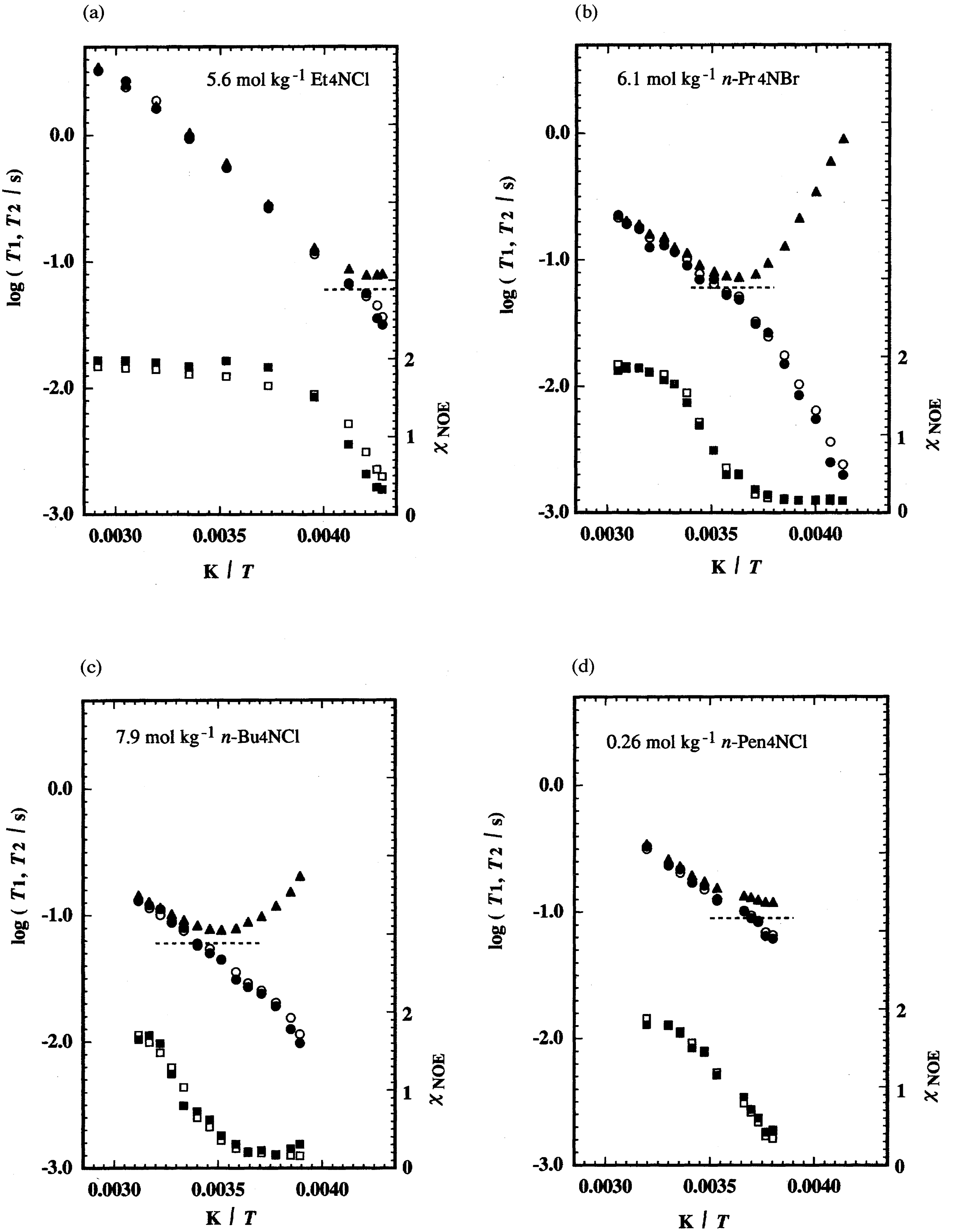

Fig. 1. Temperature dependences of T_1 (triangles), T_2 (circles), and χ_{NOE} (squares) of the α-carbon in the concentrated aqueous solutions of tetraalkylammonium salts. The solid and open symbols represent the observed and the calculated values, respectively (See text). A broken line in each figure indicates the minimum T_1 value assuming only the isotropic overall rotational motion. The resonance frequency for the measurements of the carbon-13 NMR are 100 MHz and 64 MHz respectively for n-Pen_4N^+ and for the others.

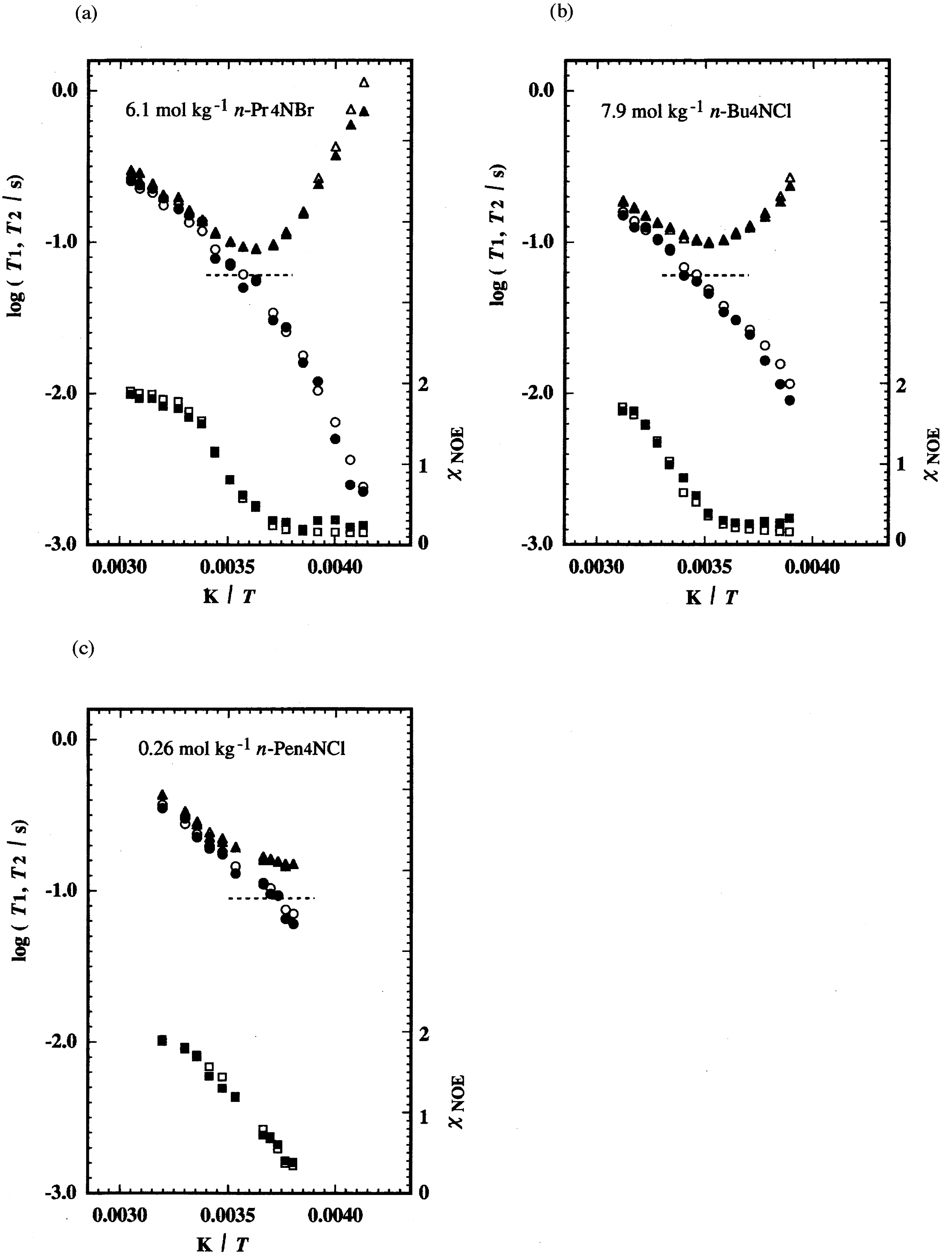

Fig. 2. Temperature dependences of T_1 (triangles), T_2 (circles), and χ_{NOE} (squares) of the β-carbon in the concentrated aqueous solutions of tetraalkylammonium salts. The solid and open symbols represent the observed and the calculated values, respectively (See text). A broken line in each figure indicates the minimum T_1 value assuming only the isotropic overall rotational motion. The resonance frequency for the measurements of the carbon-13 NMR are 100 MHz and 64 MHz respectively for n-Pen$_4$N$^+$ and for the others.

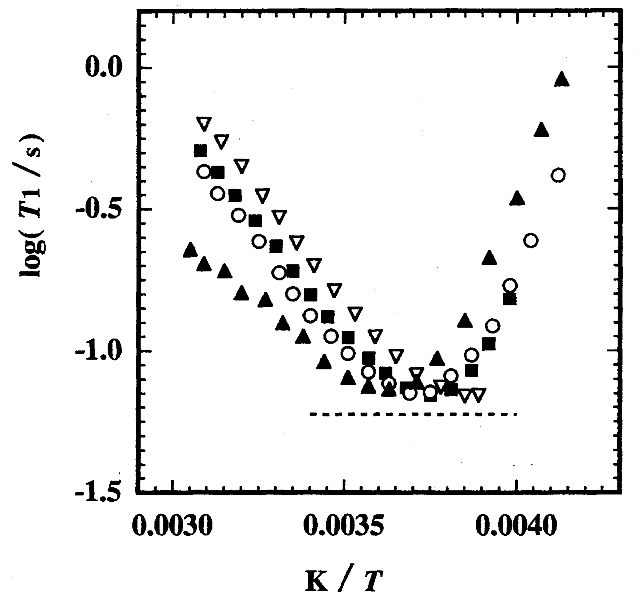

Fig. 3. Temperature dependences of T_1 of the α-carbon in the aqueous solutions of various concentrations of tetra(*n*-propyl)ammonium bromide; ▲: 6.1 mol kg^{-1}, ○: 4.3 mol kg^{-1}, ■: 3.5 mol kg^{-1}, ▽: 2.7 mol kg^{-1}. A broken line in the figure indicates the minimum T_1 value assuming only the isotropic overall rotational motion.

energy steeply increases in the molecular mechanics calculation, as shown in Fig. 5. The overall rotational correlation times, τ_r, at various temperatures can then be determined with the θ values thus obtained, if one assumes their temperature independence. These results are shown in Figs. 6 and 7.

The validity of the τ_r values obtained from the present model is confirmed by comparing the observed T_2 and χ_{NOE} values for the α-carbons with those calculated according to Eqs. 1, 2, and 4 with the θ and τ_r values obtained above. The calculated T_2 and χ_{NOE} values showed good similarity with those observed as shown in Fig. 1. Similar calculations were carried out for the T_1, T_2, and χ_{NOE} values for the β-carbons. The restricted angle, θ, for the α-C–β-C rotation for each R_4N^+ ion was determined from the T_1 minimum value for the β-carbon.[25] The T_1, T_2, and χ_{NOE} values for the β-carbon at various temperatures were then calculated using these values of the restricted angles, θ, for the β-carbon in addition to the values of θ for the α-carbon and of τ_r. As shown in Fig. 2, the T_1, T_2, and χ_{NOE} for the β-carbons thus

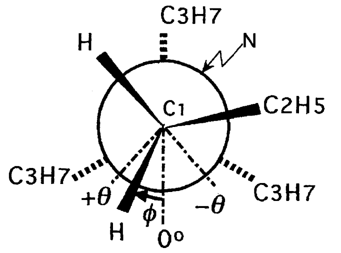

Fig. 4. Illustration of the azimuthal angle, ϕ, and the boundaries at $\pm\theta$ for the rotation around the N–α-C bonds in *n*-Pr_4N^+. Those angles are similarly defined for the rotation of the α-C–β-C bonds.

Table 2. The Restricted Angles, θ, for the Rotation around the N–α-C and α-C–β-C Bonds in the Aqueous Solutions of Various Tetraalkylammonium Salts

Compound	m/mol kg^{-1}	θ/degree	
		N–α-C	α-C–β-C
Et_4NCl	5.6	20	—
n-Pr_4NBr	6.1	16	20
	4.3	16	20
	3.5	15	19
	2.7	16	19
	1.4	16	20
n-Bu_4NCl	7.9	20	22
n-Pen_4NCl	0.26	20	20

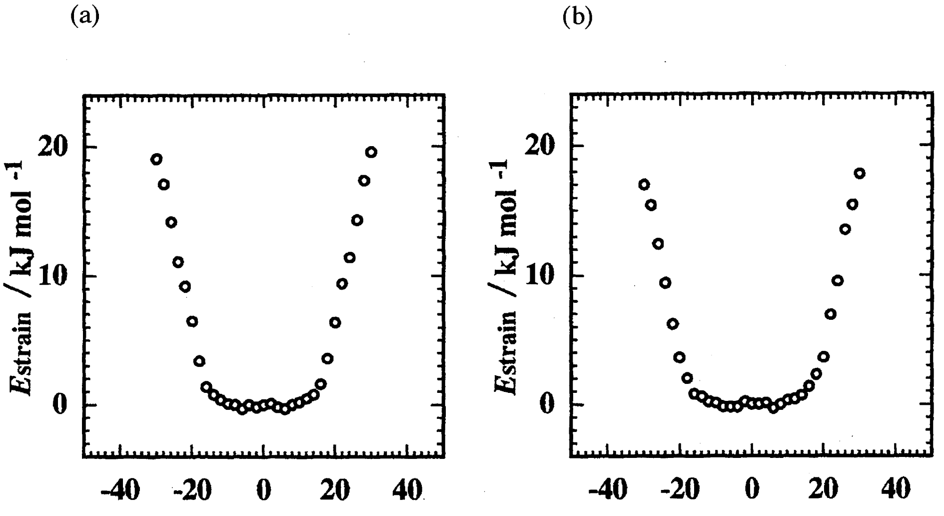
(a) (b)

Fig. 5. Total strain energies, E, in the function of the azimuthal angle, ϕ, for the rotation of (a) the N–α-C and (b) the α-C–β-C bond for *n*-Pr_4N^+ by a molecular mechanic calculation.

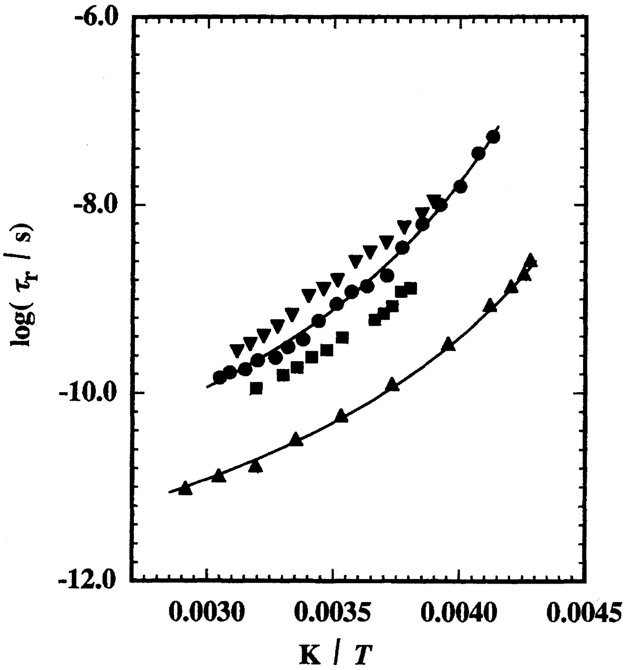

Fig. 6. Temperature dependences of the overall rotational correlation times of R_4N^+; ▲, 5.6 mol kg^{-1} Et_4NCl; ●, 6.1 mol kg^{-1} n-Pr_4NBr; ▼, 7.9 mol kg^{-1} n-Bu_4NCl; ■, 0.26 mol kg^{-1} n-Pen_4NCl. Solid lines indicate the fitted values to Eq. 5 (See text).

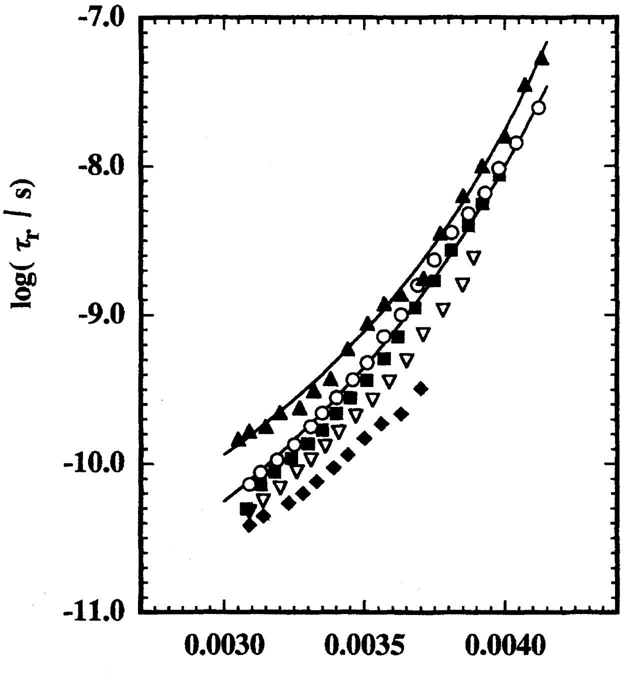

Fig. 7. Temperature dependences of the overall rotational correlation times of n-Pr_4N^+ in the aqueous solutions of the bromide; ▲, 6.1 mol kg^{-1}; ○, 4.3 mol kg^{-1}; ■, 3.5 mol kg^{-1}; ▽, 2.7 mol kg^{-1}; ◆, 1.4 mol kg^{-1}. Solid lines indicate the fitted values to Eq. 5 (See text).

calculated satisfactorily reproduced those observed, except at temperatures much lower than the T_1 minimum temperatures for the corresponding tetraalkylammonium ions.[26]

Overall Rotational Correlation Time. Figures 6 and 7 show the logarithm plots of the overall rotational correlation times of R_4N^+ versus the inverse of the temperature. The plots curve upward with decreasing temperature. In the case of the aqueous solutions of 1—5 mol kg^{-1} Et_4NCl or 4—6 mol kg^{-1} n-Pr_4NBr, a glass transition was observed.[13,14,16,27] (See Table 1). In many viscous liquids or solutions with a glass transition, the dynamic properties show non-Arrhenius temperature dependence and diverge on approaching the glass transition temperature; the temperature dependence of a dynamic quantity, X, is empirically represented by the following VTF formula.[28,29]

$$X = A\exp\{B/(T-T_0)\}, \qquad (5)$$

where A, B, and T_0 are constants and T_0 is considered to be near the glass transition temperature, T_g. For example, Lang et al. used this equation to represent the temperature dependence of the rotational correlation time of water in concentrated aqueous electrolyte solutions.[30] Considering the similarity of the system, in the present study, the obtained temperature dependences of τ_r in the aqueous solutions of 4.3 and 5.6 mol kg^{-1} of Et_4NCl and 6.5 mol kg^{-1} of n-Pr_4NBr were fitted to Eq. 5 by substituting X with τ_r. The fitting results are shown in Figs. 6 and 7, and the determined T_0 values are listed in Table 1 together with the glass transition temperatures. These T_0 values are close to the corresponding glass transition temperatures.[13,14,16]

The Rotational Correlation Time in the Dilute Solution. In the dilute tetraalkylammonium salt solutions, the τ_r values are much smaller than ω^{-1} (i.e., extreme narrowing limit, $\tau_r^2\omega^2 \ll 1$), then the observed T_1 can be expressed by:

$$\frac{1}{T_1} = K_m \alpha \tau_r. \qquad (6)$$

If the value of α in Eq. 6, i.e., θ in Eq. 4, is given, then one can obtain the τ_r value from the measured T_1 value of the α-carbon. The boundary angles, θ, i.e., α, in the dilute solutions can be regarded to be similar to those in the concentrated solutions of the corresponding tetraalkylammonium salts since no significant difference in the minimum values, i.e., in the boundary angle, θ, were observed between the solutions of the different concentrations in the case of n-Pr_4N^+, as shown in Fig. 3 and Table 2. Using these θ values, the overall rotational correlation times were then determined from the observed T_1 values for the α-carbon in the dilute R_4NX solutions.

The determined τ_r values in 0.02 mol kg^{-1} aqueous solutions of various tetraalkylammonium salts are shown in Fig. 8. These results indicate a slow-down of the rotational motions with increasing ionic sizes. Such size dependence of the rotational correlation time is qualitatively understood by the Stokes–Einstein–Debye equation and under stick hydrodynamic boundary the correlation time is represented by:[21,32]

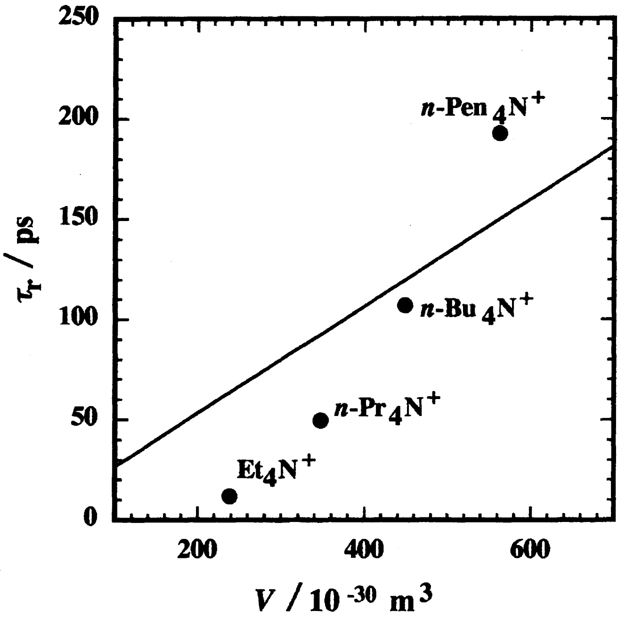

Fig. 8. Plot of the overall rotational correlation times of R_4N^+ in the 0.02 mol kg^{-1} aqueous solutions at 25 °C against the ionic volume, V. A solid line indicated the calculated values according to the Stokes–Einstein–Debye equation (Eq. 7). The values of the volumes are assumed to be equal to the partial molal volumes at infinite dilution in water given in Ref. 1.

$$\tau_r = \frac{4}{3}\pi r^3 \eta / k_B T, \tag{7}$$

where η and r represents the viscosity and the molecular (ionic) radius, respectively. However, this equation can be quantitatively applicable when a solute molecule (an ion) is large enough to regard the solvent as a continuum.[29,30] Actually, much smaller τ_r values than those predicted by Eq. 7 are reported when the sizes of a solute molecule (ion) and a solvent molecule are comparable.[32,33] The calculated τ_r values of R_4N^+ by Eq. 7 are shown by the solid line in Fig. 8. That the τ_r values observed for Et_4N^+ and n-Pr_4N^+ were smaller than those calculated can be thus understood as due to the insufficient sizes of the ions with regard to the solvent (water) as a continuum. Whereas the τ_r value of the n-Pen_4N^+ ion is significantly larger than that calculated by Eq. 7. The effect of the ionic charge of n-Pen_4N^+ on τ_r is negligibly small when the effect is estimated by the electro-hydrodynamic model (Hubbard–Onsager–Felderhof model).[34] The following two causes are considered to bring about the observed τ_r value of n-Pen_4N^+ exceeding those theoretically calculated based on the hydrodynamic (SED) or the electro-hydrodynamic (HOF) model.

(i) The tetraalkylammonium ions with large alkyl groups, such as butyl- and 3-methylbutyl, are known to form a clathrate hydrate.[19—21] The clathrate-like hydration structure, where the hydrogen bond between the water molecules around the ion is well developed, still remains at room temperature,[35] and the water molecules around the ion are less mobilized by this rigid hydration structure.[36] Thus the rotational frictions of the R_4N^+ ions are increased.

(ii) In the clathrate hydrates, four of the alkyl chains show nearly an all-*trans* conformation.[19—21] If such a stretched alkyl-chain structure is almost held in the aqueous solution, the ragged shape gives an appreciably larger rotational correlation time than that predicted by the Stoke–Einstein–Debye equation (Eq. 7).[37]

At the present time, we can not judge which contribution is the major cause that increases the rotational friction. Experiments on the rotational correlation times of R_4N^+ in dilute solutions, concerning the temperature dependence and those in different solvents, are currently in progress.

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$$J(\omega_i) = \alpha_\alpha \alpha_\beta \frac{\tau_r}{1+\tau_r^2\omega_i^2},$$

where α_α and α_β represent the α in Eq. 4 with the restricted angle around the N–α-C and α-C–β-C bonds, respectively.[24)]

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