J. Phys. Chem. A **2001,** *105,* 2989−2996

Solvent Effect on Rotational Relaxation Time of Ammonium Ion

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Received: September 16, 2000; In Final Form: January 3, 2001

The rotational relaxation times of ammonium ion, τ_{2r}, in 11 solvents were determined by the measurements of the ^{15}N NMR spin-lattice relaxation times and the nuclear Overhauser enhancement (NOE) factors under the condition of negligible ion−ion interaction. The observed solvent dependence of the rotational relaxation times showed a poor correlation with those for predicted from a hydrodynamic (Stokes−Einstein−Debye) model or an electro hydrodynamic (Hubbard−Onsager−Felderhof) model, whereas a much better linear relation was found for the plot of the logarithms of the observed rotational relaxation times versus Gutmann's solvent donor numbers. The results of these solvent dependence trends were compared with those perchlorate rotation, and the difference in the validity of the continuum models between the rotational motions of these two ions was discussed. A comparison was also made between the solvent dependences of the rotational and the translational diffusion of the ammonium ion.

1. Introduction

Ionic rotation and translation are important probes to elucidate how solvent macroscopic or microscopic properties contribute to various dynamic processes in solution.[1,2] However, ionic rotation would be in contrast to ionic translation in terms of the response to the solvent since the rotational motion does not always require solvent displacement, which is indispensable for the translation, and properties of the solvent as a hydrodynamic or a dielectric continuum, therefore, contribute to the rotation in a different manner from the translation. For example, under perfect slip boundary condition in the hydrodynamic regime, the hydrodynamic friction becomes zero for the rotation of a spherical molecule (ion) and is $4\pi R\eta$ for the translation (R and η being the radius and the solvent viscosity, respectively).[3] Due to such a weak contribution from the hydrodynamic friction to the rotation the rotational motion is expected to be a sensitive probe for examining the effect of solvent at a molecular level.

The effect of solvent on the rotational motion of a (spherical) ion is also important as an analogy of that on ultrafast intramolecular charge (proton and electron) transfer reactions if the ionic rotation is regarded as a fractional charge migration within the sphere of the ion by considering the charge distribution within the ion. The dynamical solvent effect on both the rotational relaxation times and the charge-transfer reaction rates is then reduced to the dynamical response of the solvent polarization to the charge migration during the course of the ionic rotation and of the barrier crossing of the reaction,[4,5] respectively, without pushing aside solvent.

Studies on ionic rotation in solution have been performed for many kinds of ions from various points of view, e.g., inorganic ions such as NO_3^-,[6−10] CO_3^{2-},[9] XO_4^{n-} (X = Cl, S, P),[11,12] and NH_4^+,[13] and some metal complex ions.[14,15] On the other hand, examples for systematic experiments on the rotational motions of spherical ions in a wide variety of solvents and tests by various continuum models are very limited. Such a study is, however, indispensable to clarify the limitation to regarding the solvent as a hydrodynamic and dielectric continuum and requiring the introduction of "molecularlity" of the solvent.

In the present study, we examined the solvent dependence of the rotational relaxation time of ammonium ion and compared the results with that of perchlorate ion. In our previous study on the rotational motion of the perchlorate ion,[12] it was shown that hydrodynamic or electrohydrodynamic models well represent, at least phenomelogically, the rough trend of the observed solvent dependence of the rotational relaxation times, despite the size of the ion being not large enough to regard the solvent as a hydrodynamic and/or a dielectric continuum. The ammonium ion is the smallest spherical ion that has a freedom of rotation. The solvent effect on the rotational relaxation time is of particular interest for comparison with the perchlorate ion from the following points of view: (i) within the framework of solvent continuum models, the smaller size of the ammonium ion makes the hydrodynamic friction for the rotation less important, and (ii) the larger surface charge density increases the contribution of the dielectric friction or site−site interactions between the ammonium protons and solvent molecules.

The rotational relaxation times of the ammonium ion were determined by measurements of the spin−lattice relaxation times of the ^{15}N nucleus. This method gives the rotational relaxation time without any ambiguity because we can determine the contribution of the magnetic dipolar interaction to the spin-lattice relaxation time by NOE measurements. The rotational relaxation times of the ammonium ion by this method have already been reported by Perrin et al.[13] Although they compared the obtained rotational relaxation times in various solvents with various solvent parameters, e.g., the viscosity, dielectric constant, dipole moment, and proton acceptor abilities, etc., no obvious correlation was found, and the data did not clarify the origin of the rotational relaxation time of the solvent dependence. These results may have occurred, at least partially, for the following reasons: (i) the variation in the solvent was limited to highly polar solvents, and (ii) the concentrations of the ammonium salts were relatively high. (ca. 0.1−1.4 mol L^{-1}). As pointed out in

10.1021/jp003300b CCC: $20.00

our previous study for the solvent dependence of the rotational relaxation times of the perchlorate ion,[12] a choice of solvents with wide variations in solvent properties is particularly effective for judging the validity of solvent continuum models. The interaction with a counteranion also disturbs the analysis of the solvent dependence; e.g., the ion-pair formation will change the rotational relaxation time.[14,15] The extent of this contribution will depend on the solvent since the formation constant depends on the solvent properties, such as the dielectric constant. In the present study, we used 11 solvents, which were chosen account for wide variations in dielectric constant and viscosity, etc. The concentration of the ammonium salt (ammonium perchlorate) was adjusted as low as possible to prevent any ion−ion interaction (decreased to 0.015 mol L $^{-1}$).

2. Experiments

NMR Measurements. The NMR spin-lattice relaxation times, T_1, were obtained using a JEOL GSX-400 Fourier transform spectrometer operating at 40.52 MHz for ^{15}N and 61.37 MHz for ^{2}D (9.4 T) with 10 mm (o.d.) Pyrex tubes. The T_1 values were measured by the inversion recovery method with a pulse sequence of (π pulse − Δt − $\pi/2$ pulse)$_n$.

For the ^{15}N T_1 measurements, the free induction decay signals were accumulated, e.g., about 200 times for each Δt for a solution of 0.015 mol L^{-1} 99 atom % enriched $^{15}NH_4ClO_4$ and 7−12 different Δt were used. (the maximum Δt being ca. 5T_1) The observed T_1 values were reproduced within ±5−10% for the repetition of the T_1 measurements (3−5 times). For the ^{15}N T_1 measurements in nitromethane, the T_1 value increased to more than 200 s, and it may take more than a week for the entire T_1 measurement run. In this case, we carried out the measurements of $M(\infty)$ just after each $M(\Delta t)$ measurement considering the instability of the spectrometer or magnetic field during the entire T_1 measurement run. ($M(x)$ is the ^{15}N signal intensity with $\Delta t = x$ and assuming $M(\infty) \approx M(3T_1)$ in this case.)

The factors of the nuclear Overhauser enhancement, χ_{NOE}, were measured using a gated decoupling method. The values were determined from four or more sets of peak areas with and without NOE. The estimated error in χ_{NOE} was ±0.1 or less.

To confirm the maximum concentration of the ammonium salt, where the effect of the interaction with the counter perchlorate anion on the rotational relaxation time of the ammonium ion can be negligible, the ^{2}D T_1 was measured for the 0.002−0.05 mol L^{-1} deuterated ammonium perchlorate in acetone, instead of the measurements of the ^{15}N T_1 since the ^{15}N measurements required an extremely long time at low concentrations because of the lower sensitivity and the longer T_1. (vide supra) For the ^{2}D T_1 measurements, the free induction decay signals were accumulated, e.g., about 100−200 times for each Δt for a solution with a 0.01 mol L^{-1} ammonium salt concentration and 20−25 different Δt values (the maximum Δt being about 10 T_1) were used. The experimental error was estimated to be ±5% by the results of repetition of the T_1 measurements (3−5 times). In dilute solutions (> ca. 0.01 mol L^{-1}), a slight nonlinear behavior was observed in some solvents for plots of the log(($M(\infty) - M(\Delta t)$)/2$M(\infty)$) versus Δt ($M(x)$ being the ^{2}D signal intensity with $\Delta t = x$), which is attributed to a magnetization exchange effect by the deuteron exchange of ND_4^+ with deuterons of trace amount of water in the solvent. In this case, the T_1 value of the ammonium ion was determined by fitting the observed Δt dependent signal intensity, ($M(\infty) - M(\Delta t)$)/2$M(\infty)$), to the analytical formula presented by Ichikawa et al.[16] The ammonium T_1 value and the deuteron exchange rate were treated as adjustable parameters. The ratio of the fraction of deuterons in the ammonium ion and water in the sample solution was determined by integration of the respective ^{2}D signals. The ^{2}D T_1 values of water were measured in solutions without the ammonium salt.

Temperature was controlled within 25 ± 0.5 °C with a JEOL GVT2 temperature control unit. The temperature increase in the sample solutions due to proton irradiation was minimized by adjusting the irradiation power as low as possible. The temperature elevation due to the proton irradiation was 0.5 °C at the maximum.

Protiated solvents were used for the ^{15}N and ^{2}D NMR measurements and were purchased from Wako Chemicals Co., Ltd., (analytical grade) except for hexamethylphosphoric triamide (HMPA) from Aldrich Chemical Co., Ltd. The solvents were dried prior to use by standard methods.[17] The sample solutions were degassed by a freeze−thaw cycle and then sealed under vacuum.

Materials. 99% ^{15}N-enriched ammonium chloride purchased from MSD Isotopes was treated by an ion-exchange resin (Dowex 1-X8), which was converted to the perchlorate form. The ^{15}N-enriched ammonium perchlorate thus obtained was purified by two recrystallizations from water. The deuterated ammonium perchlorate was obtained by two recrystallizations of the protiated ammonium perchlorate in D_2O.

3. Results

3.1. Evaluation of the Rotational Relaxation Time of Ammonium Ion. The ^{15}N and ^{2}D spin-lattice relaxation time measurements will be used to determine the rotational relaxation times of the ammonium ion.[18]

The ^{15}N spin lattice relaxation time, $T_{1,\mathrm{dd}}$(N), caused by the magnetic dipole−dipole interaction with the protons attached to the ^{15}N atom depends on the rotational relaxation time associated with the second rank of spherical harmonics, $\tau_{2\mathrm{r}}$, (see eq 1a). The contribution of the dipolar interaction to the observed spin-lattice relaxation time, $T_{1,\mathrm{obs}}$(N), is determined by measurements of the nuclear Overhauser enhancement factor, χ_{NOE}, as shown in eq 1b at the extreme narrowing limit.[19]

$$\frac{1}{T_{1,\mathrm{dd}}(\mathrm{N})} = n\gamma_{\mathrm{N}}^2\,\gamma_{\mathrm{H}}^2\hbar^2 r_{\mathrm{NH}}^{-6}\tau_{2r} \tag{1a}$$

$$\frac{1}{T_{1,\mathrm{dd}}(\mathrm{N})} = \frac{\chi_{\mathrm{NOE}}}{-4.93}\,\frac{1}{T_{1,\mathrm{obs}}(\mathrm{N})} \tag{1b}$$

where γ_{N} and γ_{H} represent the gyromagnetic ratios of ^{15}N and ^{1}H nuclei, respectively. n and r_{NH} indicate the number of protons attached to the ^{15}N atom ($n = 4$) and the N−H bond length, respectively, and the latter is taken to be 1.01 Å.[20]

The magnetic relaxation of the ^{2}D nucleus ($I = 1$) is caused by the so-called quadrupole interaction, i.e., the interaction between the electric quadrupole moment of the nucleus and the electric field gradient at the nucleus.[21,22] The deuteron spin-lattice relaxation time, T_1(D), at the extreme narrowing limit is then expressed by[21,22]

$$T_1(\mathrm{D})^{-1} = \frac{3}{40}\,\frac{2I+3}{I^2(2I-1)}\left(1+\frac{\alpha^2}{3}\right)\left(\frac{e^2Qq}{\hbar}\right)^2\tau_{\mathrm{c}} \tag{2}$$

where eQ, eq, and α represent the quadrupole moment of the ^{2}D nucleus ($Q = -2.73 \times 10^{-27}$ cm^2),[23] the main axis component of the electric field gradient (efg) at the ^{2}D nucleus,

TABLE 1: ^{15}N NMR Results and Rotational Relaxation Times of Ammonium Ion in Various Solvents and Their Physical Properties at 25 °C

solvent	T_1^{-1}/s^{-1} [a]	χ_{NOE}[a]	T_{1dd}^{-1}/s^{-1} [a]	τ_{2r}/ps[a]	viscosity/cP[b]	ϵ_0[c]	ϵ_∞[c]	τ_D/ps[c]
1. nitromethane	0.005	−4	0.005	0.3	0.627	36 d	2[d]	2[d]
2. acetone	0.021	−4.2	0.018	0.87	0.300	20.7[d]	1.9[d]	2[d]
3. acetonitrile	0.013	−4.2	0.011	0.53	0.339	37.5[e]	2[e]	3.3[e]
4. propylene carbonate	0.023	−4.4	0.021	1.03	2.530	65[e]	4.1[e]	43[e]
5. dimethyl sulfoxide (DMSO)	0.13	−4.9	0.13	6.3	1.960	46.6[e]	5.7[e]	19.5[e]
6. *N,N′*-dimethyl-formamide (DMF)	0.075	−4.6	0.071	3.4	0.796	36.7[e]	4.5[e]	11[e]
7. hexamethylphosphoric-triamide (THMPA)	0.71	−4.4	0.63	31	2.350	29.6[d]	3.3[d]	80[d]
8. water	0.020	−4.7	0.019	0.93	0.890	78.3[f]	5.2[f]	8.2[f]
9. methanol	0.077	−4.5	0.070	3.4	0.542	32.7[e]	5.6[e]	48[e]
						32.5[g,h]	25[g,h]	51.5(0.89), 7.1(0.04), 1.1(0.01)[g,h]
10. ethanol	0.24	−4.5	0.22	5.8	1.078	24.5[e]	4.2[e]	130[e]
						24.3[g,h]	2.7[g,h]	163(0.93), 8.9(0.04), 1.8(0.05)[g,h]
11. ethylene glycol	0.27	−4.6	0.25	12.4	16.2	37.9[i]	2.3[i]	105[i]
						37.9[i,j]	2.0[i,j]	124(0.93), 12.2(0.07)[i,j]

[a] The concentration of the anmmonium perchlorate is 0.015 mol L^{-1}. [b] The data other than nitromethane are taken from: Viswanath, D. S.; Natarajan, G. *Viscosity of Liquids*; Hemisphere: New York, 1989. The value of nitromethane is taken from: Ridick, A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents, Physical Properties and Methods of Purification*; Wiley: New York, 1986. [c] Assuming single dielectric relaxation unless otherwise stated. [d] Nielson, R. M.; McManis, G. E.; Golovin, M. N.; Weaver, M. J. *J. Phys. Chem.* **1988**, *92*, 3441. [e] McManis, G. E.; Golovin, M. N.; Weaver, M. J. *J. Phys. Chem.* **1986**, *90*, 6563. [f] Evans, D. F.; Tominaga, T.; Hubbard, J. B.; Wolynes, P. G. *J. Phys. Chem.* **1979**, *83*, 2669. [g] Triple relaxation is assumed. The values in parentheses are amplitude factors for the corresponding relaxations. [h] Maroncelli, M. J. *Mol. Liq.* **1993**, *57*, 1. [i] Double relaxation is assumed. The values in parentheses are amplitude factors for the corresponding relaxations. [j] MacManis, G. E.; Weaver, M. J. *J. Chem. Phys.* **1989**, *90*, 912.

and the asymmetry parameter, respectively. τ_c is the correlation time of the fluctuation of the field gradient. If the efg is caused by the N−D bond formation, the τ_c value is then equal to the rotational relaxation time of the ammonium ion, τ_{2r}.[21,22] The surrounding solvent (molecules), however, provides a minor but not negligible effect on the T_1 (D) value because of an additional electric field gradient caused by the surrounding solvent dipoles.[11,21,24] For example, the ratio of the observed values, $T_1(D)^{-1}/T_{1,dd}(N)^{-1}$, in HMPA is about 40% greater than that in acetone. [25] Therefore, the evaluation of the rotational relaxation times, τ_{2r}, from the ^{2}D T_1 measurement is inappropriate for the comparison of the τ_{2r} values over the wide variation in solvents. An application of the ^{2}D T_1 measurements is also inappropriate in protic solvents because of the proton (deuteron) exchange with the solvents.

Thus, we used the ^{15}N T_1 and χ_{NOE}, measurements for the determination of the rotational relaxation times in the various solvents. On the other hand, the experiments should be carried out at an ammonium perchlorate concentration as low as possible in order to prevent any effect of the counteranion (perchlorate ion) on the rotational relaxation time. The ^{15}N T_1 measurement is, however, quite difficult at an ammonium perchlorate concentration lower than ~0.01 mol L^{-1} because it requires an extremely long time.[26] For this reason, we roughly estimated the concentration dependence of τ_{2r} unitil the very low concentrations (~0.002 mol L^{-1}) by the ^{2}D T_1 measurements due to the ease of the measurement,[26] and, then, the maximum concentration, where the effect of the perchlorate anion is practically negligible, was determined as 0.015 mol L^{-1}. (See Section 3.2)

Thus we measured the ^{15}N T_1 and χ_{NOE}, at 0.015 mol L^{-1} ammonium perchlorate concentration and obtained the rotational relaxation times in various solvents. The values are listed in Table 1.

3.2. Estimation of the Concentration Dependence of the Rotational Relaxation Time. The ^{2}D spin-lattice relaxation times of the deuterated ammonium ion (at the perchlorate concentration of 0.002−0.05 mol L^{-1}) were measured instead of those for ^{15}N for the purpose of a rough estimation of the concentration dependence of the rotational relaxation time, as mentioned in Section 3.1.

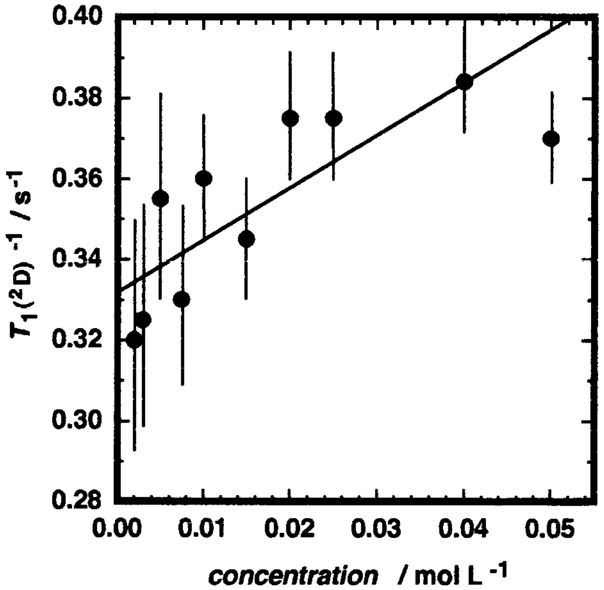

Figure 1. Dependence of the inverse of the ^{2}D spin-lattice relaxation times of the ammonium ion, $T_{1(D)}^{-1}$, on the concentration of ammonium perchlorate in acetone at 298 K. The solid line indicates the least-squares fitting result assuming a linear relationship below 0.02 mol L^{-1}.

Figure 1 shows the dependence of the $T_1(D)^{-1}$ values of the ammonium ion on the concentration in acetone. A linear concentration dependence in τ_{2r} was observed in some ions in the dilute solutions (0.02 − 0.1 mol L^{-1}),[12,27,28] and was theoretically predicted by Ibuki et al.[29] In the present study, the effect of the perchlorate anion on the τ_{2r} values, i.e., the $T_1(D)^{-1}$ values below the perchlorate salt concentration of 0.015 mol L^{-1} was, however, not beyond 10% of the value extrapolated to infinite dilution if a linear relation was assumed to the concentration dependence of τ_{2r}, i.e., $T_1(D)^{-1}$ below 0.02 mol L^{-1}. The effect of the counteranion on τ_{2r} is expected to be the largest in acetone because the dielectric constant of acetone is the smallest among the solvents used in the present study. Consequently, the τ_{2r} values at 0.015 mol L^{-1} were regarded as those at infinite dilution for all the solvents, considering the experimental error in the ^{15}N T_1 measurements.

3.3. Application of the Continuum Models for the Ammonium Rotation. The rotational relaxation times obtained in the various solvents at 298 K are listed in Table 1 together with some solvent properties. The solvent dependence of the rotational relaxation time was compared with those predicted by the following models, where the solvent was regarded as a hydrodynamic and/or a dielectric continuum.

Hydrodynamic Model. The Stokes−Einstein−Debye (SED) equation is one of the simplest representations for molecular (ionic) rotation, where a molecule (ion) and a solvent are characterized by a rigid sphere with radius R and a continuum viscous fluid with viscosity η, respectively, i.e., the ionic charge and the solvent dielectric properties are disregarded.[30,31] The hydrodynamic friction, ζ_r(SED), or the rotational relaxation time, τ_{2r}, for a rotating sphere is then represented by[30]

$$\zeta_r(\mathrm{SED}) = C(8\pi R^3)\eta \tag{3a}$$

and

$$\tau_{2r}(\mathrm{SED}) = \frac{\zeta_r(\mathrm{SED})}{6k_BT} = C\left(\frac{4}{3}\pi R^3\right)\eta/k_BT \tag{3b}$$

where k_B is the Boltzmann constant, T is the absolute temperature, and C is a constant associated with the hydrodynamic boundary condition; for a spherical rotor, $C = 1$ for the stick boundary, and $C = 0$ for the slip boundary.

The closed circles in Figure 2 indicate a plot of the logarithms of the observed τ_{2r} values of the ammonium ion in various solvents at 298 K versus those calculated according to eq 3b assuming the stick boundary, i.e., $C = 1$, together with the results for the perchlorate rotation as shown by the open triangles. The plot for the ammonium ion showed a quite poor correlation compared with that for the perchlorate. On the other hand, the values for the ammonium ion are much longer than those for the perchlorate ion in most of the solvents used in the present study and were more similar to those predicted by the SED model assuming a stick boundary. This slowdown in the ammonium rotation may indicate the importance of the interaction between the solvent and the ionic charge or the fractional charge of the ammonium protons. This observation should be contrasted to the prediction that the relaxation is faster than that of perchlorate, since a spherical molecule (ion) with a size comparable or smaller than that of the solvent should have a more “slip” boundary condition.[31,32]

Hubbard−Onsager−Felderhof Electro-Hydrodynamic Model. In the SED model, the interactions between the ionic charge and dielectric properties of the solvent are disregarded. The effect of the ionic charge on the friction of the ionic rotation is treated by Felderhof,[33] where coupling of the hydrodynamic and the dielectric effects is taken into account based on the Hubbard−Onsager electro-hydrodynamic model.[34] The rotational relaxation time for a spherical ion with ionic charge, z, is then represented by[33]

$$\tau_{2r}(\mathrm{HOF}) = \left(\frac{4}{3}\pi R^3\right)\left(\frac{\eta}{k_BT}\right)\left(\frac{1}{1 - CJ(u)}\right) \tag{4a}$$

$$J(u) = 1 - \frac{3}{4u^3\sqrt{2}}\left[2\pi - \arctan\left(\frac{u\sqrt{2}}{u^2 - 1}\right) - \ln\left(\frac{1 + u\sqrt{2} + u^2}{1 - u\sqrt{2} + u^2}\right)\right] \tag{4b}$$

$$u = R_{HO}/R \tag{4c}$$

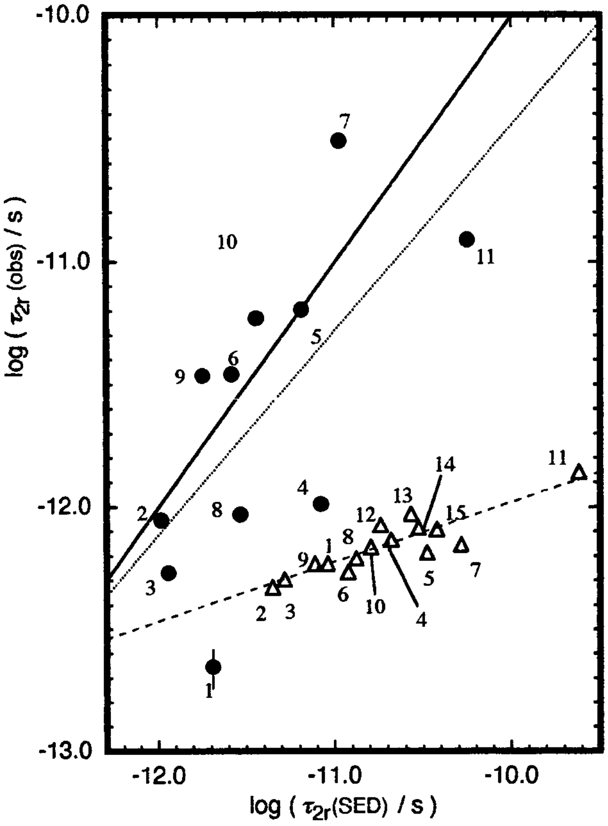

Figure 2. Logarithm plot of the observed τ_{2r} values of the ammonium ion (closed circles) and of the perchlorate ion (open triangles) versus those calculated by the Stokes−Einstein−Debye equation assuming the stick hydrodynamic boundary condition at 298 K. The data for the perchlorate ion were taken from ref 12. Numbers in the figure indicate the solvent used: (1) nitromethane; (2) acetone; (3) acetonitrile; (4) propylene carbonate; (5) dimethylsulfoxide (DMSO); (6) *N*,*N*-dimethylformamide (DMF); (7) hexamethylphosphoric triamide (HMPA); (8) water; (9) methanol; (10) ethanol; (11) ethylene glycol; (12) benzonitrile; (13) nitrobenzene; (14) *n*-propanol; (15) tetramethylurea. The solid line in the figure represents the slope of unity. The dotted and the broken line indicate the least-squares fitting results assuming a linear relationship between the observed and the calculated log τ_{2r} values with the slope of 0.94 for the ammonium and with the slope of 0.25 for the perchlorate ion, respectively. The ionic radii of the ammonium and the perchlorate ion are assumed to be 1.48 and 2.40 Å for the calculations, respectively. The error bars of the data were similar or smaller than the symbols except for that in nitromethane.

where C is the parameter for the hydrodynamic boundary condition whose meaning is the same as that in the SED model. R_{HO} is the Hubbard−Onsager radius and is given by

$$R_{HO} = \left[\frac{z^2e^2}{16\pi\eta\epsilon_0{}^2}(\epsilon_0 - \epsilon_\infty)\tau_D\right]^{1/4} \tag{5}$$

where e_0, e_∞, and τ_D are the static and high-frequency dielectric constants and the dielectric relaxation time of the solvent, respectively.

Figure 3 shows the logarithm plot of the observed τ_{2r} values of the ammonium ion in various solvents at 298 K versus those calculated according to the Hubbard−Onsager−Felderhof (HOF) model together with the results for the perchlorate rotation. The plot indicates a large scattering and is similar to the case for application of the SED model.[35,36]

Dielectric Friction for a Rotating Multipole. The fractional charge on the ammonium protons is relatively large (+0.35e).[20] Such a charge distribution within an ion is disregarded in the

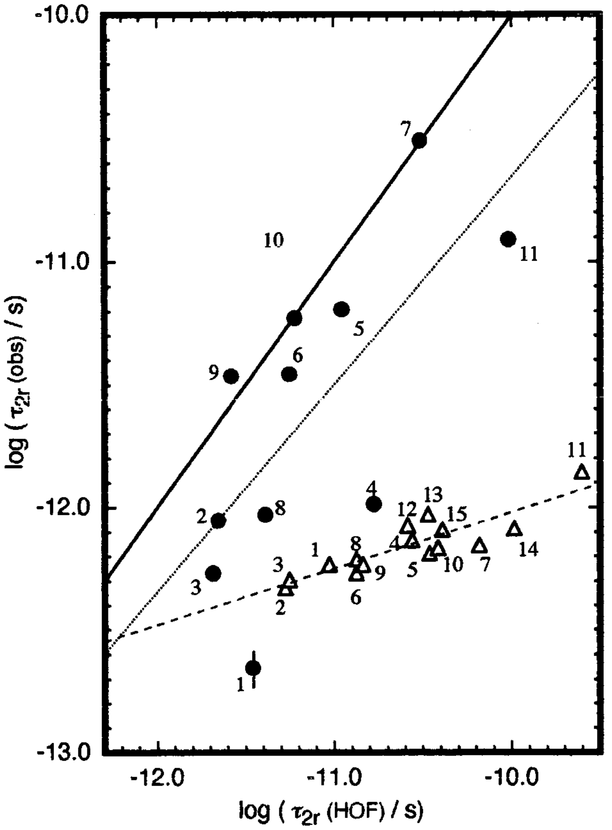

Figure 3. Logarithm plot of the observed τ_{2r} values of the ammonium ion (closed circles) and of the perchlorate ion (open triangles) versus those calculated by the Hubbard–Onsager–Felderhof model assuming the stick hydrodynamic boundary condition at 298 K. The data for the perchlorate ion were taken from ref 12. The values in alcohols were calculated with the two shorter (for methanol, ethanol, and *n*-propanol) or the shortest (for ethylene glycol) relaxation times assuming the multiple relaxations, respectively (see ref 35). The number assigned to each solvent is the same as that in Figure 2. The solid line in the figure represents the slope of unity. The dotted and the broken line indicate the least-squares fitting results assuming a linear relationship between the observed and the calculated log τ_{2r} values with the slope of 0.94 for the ammonium and with the slope of 0.23 for the perchlorate ion, respectively. The ionic radii of the ammonium and the perchlorate ion are assumed to be 1.48 and 2.40 Å for the calculations, respectively. The error bars of the data were similar or smaller than the symbols except for that in nitromethane.

electro-hydrodynamic HOF model as well as the hydrodynamic SED model. The dielectric friction for the rotation of the ammonium ion, which can be regarded as an rotational octapole considering the four protons with positive fractional charges, can be calculated by eq 6 given by Alavi and Weldick,[37] which is an extension of the dielectric friction for a rotating dipole given by Nee and Zwanzig.[38]

$$\tau_{2r}(\mathrm{AW}) = \left(\frac{1}{6k_{\mathrm{B}}T}\right)\left(\frac{2\tau_{\mathrm{D}}}{a}\right)\sum_{j=1}^{N}\sum_{i=1}^{N}\sum_{L=1}^{\infty}\sum_{M=1}^{L}\left(\frac{2L+1}{L+1}\right)\times \left[\frac{\epsilon_0-\epsilon_\infty}{\left(\epsilon_0+\epsilon_\infty\dfrac{L}{L+1}\right)^2}\right]\frac{(L-M)!}{(L+M)!}M^3q_iq_j\left(\frac{r_i}{a}\right)^L\left(\frac{r_j}{a}\right)^L\times P_L^{M}(\cos\theta_i)P_L^{M}(\cos\theta_j)\cos M\phi_{ji} \quad (6)$$

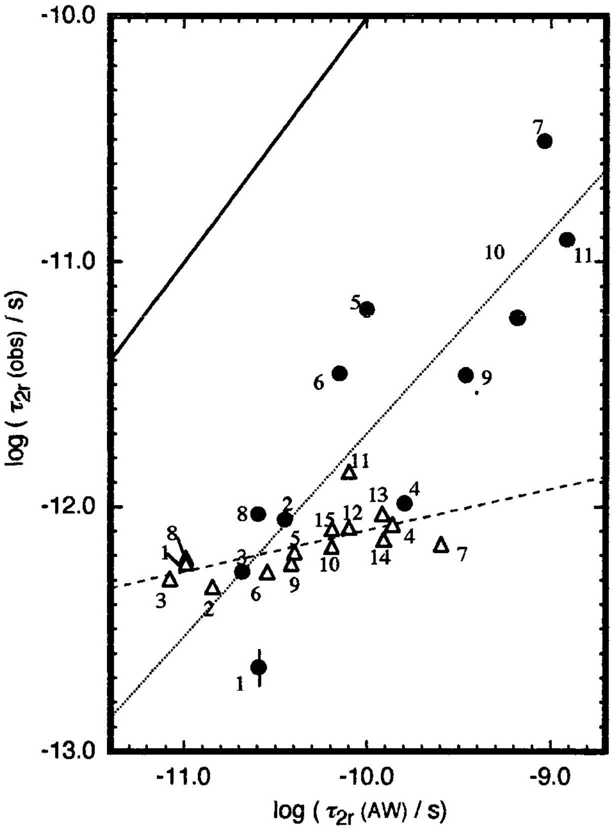

Figure 4. Logarithm plot of the observed τ_{2r} values of the ammonium ion (closed circles) and of the perchlorate ion (open triangles) versus those calculated by the Alavi–Waldeck model at 298 K. The data for the perchlorate ion were taken from ref 12. The values in alcohols were calculated with the two shorter (for methanol, ethanol, and *n*-propanol) or the shortest (for ethylene glycol) relaxation times assuming the multiple relaxations, respectively. (see ref 35) The number assigned to each solvent is the same as that in Figure 2. The dotted and the broken line indicate the least-squares fitting results assuming a linear relationship between the observed and the calculated log τ_{2r} values with the slope of 0.96 for the ammonium and with the slope of 0.17 for the perchlorate ion, respectively. The ionic radii, the N–H or Cl–O bond lengths, and the fractional charge on each hydrogen or oxygen atom are assumed to be 1.48 Å, 1.01 Å, and 0.35e, respectively, for ammonium ion, and 2.40 Å, 1.46 Å, and −0.44e, respectively, for perchlorate ion. The error bars of the data were similar or smaller than the symbols except for that in nitromethane.

where $P_L^M(x)$ are the Legendre polynomials, a is the cavity radius, N is the number of fractional charges, and q_i is the fractional charge on atom i with position (r_i, θ_i, ϕ_i) and $\phi_{ij} \equiv \phi_j - \phi_i$.

The closed circles in Figure 4 show a logarithm plot of the observed rotational relaxation times of the ammonium ion versus those calculated on the basis of the AW model. The correlation of the plot is somewhat better than those for the SED or HOF models; $r^2 = 0.44$, 0.48, and 0.72 for the SED, HOF, and AW plots, respectively (r denoting the correlation factor). These results suggest that the interaction of the fractional charge of the ammonium ion with solvent is important for the rotational friction. A comparison of the results in Figure 4 with the same plot for the perchlorate ion is worth noting. As shown by the open triangles in Figure 4, a significant positive deviation of the observed τ_{2r} value in ethylene glycol, which is a highly viscous solvent, is found in the plot for the perchlorate rotation. This result indicates that the hydrodynamic friction contributes to the rotational motion of the perchlorate ion to some extent since the hydrodynamic friction is disregarded in the calculation

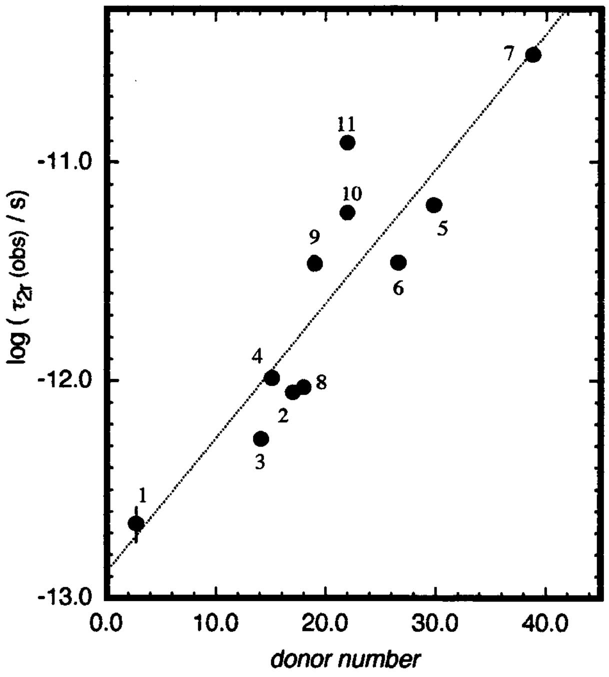

Figure 5. Plot for the logarithms of the observed τ_{2r} values of the ammonium ion versus Gutmann's solvent donor numbers at 298 K. The dotted line indicates the least-squares fitting result assuming a linear relationship. The estimated value was used for the donor number of ethylene glycol (ref 39(b)). The error bars of the data were similar or smaller than the symbols except for that in nitromethane.

based on the AW model. Such a particular deviation in ethylene glycol in the AW plot is not shown for the ammonium ion as in Figure 4, indicating that the dielectric friction for the rotation as a rotating octapole sufficiently exceeds the hydrodynamic friction.

3.4. Effect of Solvent Molecularity on the Rotational Motion. The application of solvent conntinuum models do not sufficiently work to explain the solvent dependence of the rotational relaxation of the ammonium ion. The significant negative deviations in the observed τ_{2r} in nitromethane and propylene carbonate compared with the other solvents were found in the plot for the HOF or AW models, where the solvent is regarded as a dielectric continuum (see Figures 3 and 4). For these solvents, the donor power to a positive site of solute (ammonium protons) is particularly low considering their solvent dielectric constants. Therefore, the local interaction, e.g., between the annmonium proton and a negative site of the solvent molecule, should be responsible for controlling the solvent dependence on τ_{2r}. Figure 5 shows a plot of the logarithms of the observed rotational relaxation times of the ammonium ion versus Gunmann's donor numbers of the solvent. The plot shows a much better linear correlation ($r^2 = 0.92$) compared with the other plots for the ammonium rotation. The Gutmann's donor number is a measure of the free energy of the solvent donor ability to the positive site of a solute.[39] The linear correlation in Figure 5 indicates that the rotation is achieved by surmounting the interaction barrier between the proton(s) and a negative site of the solvent molecule(s). This feature is in contrast to the case of the perchlorate rotation,[12] i.e., no correlation in the plot of the logarithm of the perchlorate τ_{2r} versus the solvent acceptor number. A meaningful positive deviation of the observed τ_{2r} value in ethylene glycol is found in Figure 5. This may be attributed to a contribution of hydrodynamic effect because of the extremely high viscosity of the solvent.

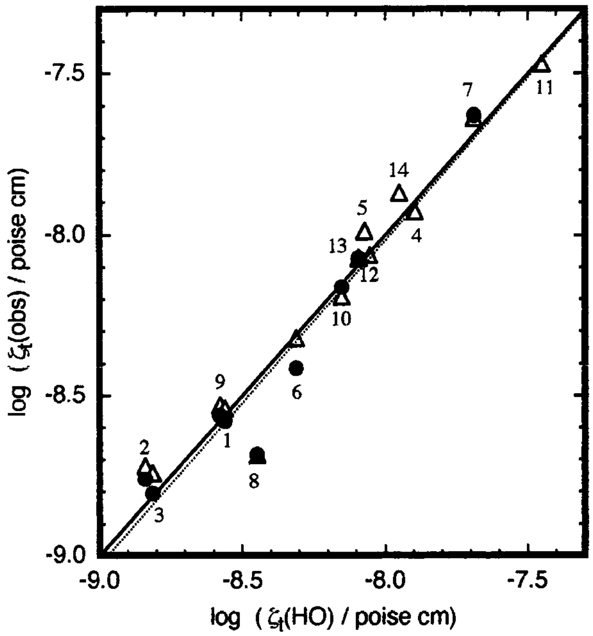

Figure 6. Logarithm plot of the translational friction coefficients obtained from the limiting values of the electric conductances of the ammonium ion, ζ_t(obs), (closed circles) versus those calculated by the Hubard−Onsager model in various solvents at 298 K assuming the slip boundary, ζ_t(HO). The observed values for the potassium ion are also plotted by open triangles. The values in alcohols are calculated with the two shorter (for methanol, ethanol, and *n*-propanol) or the shortest (for ethylene glycol) relaxation times assuming the multiple relaxations, respectively (see ref 35). The number assigned to each solvent is the same as that in Figure 2. The solid line in the figure represents the slope of unity. The dotted line in the figure indicates the least-squares fitting result assuming a linear relationship with a slope of 0.99. The values of the limiting conductances are taken from refs 40 and 41.

3.5. Comparison with the Translational Motion. It is interesting to explore the difference in the contributions to the friction for rotational and the translational motions, as mentioned in Section 1. For this purpose, the logarithms of the translational friction coefficients obtained with the observed limiting ionic conductances of the ammonium ion[40,41] by a relation, $\zeta_t(\text{obs}) = eF/\lambda_o$ (F and λ_o being the Faraday constant and the ionic limiting conductance, respectively), are plotted in Figure 6 against those calculated based on the Hubbard−Onsager electro-hydrodynamic model according to an expression given in the literature.[42,43] A similar plot for the potassium ion, whose limiting ionic conductance is similar to that of the ammonium ion,[40,41] is also made in Figure 6 in order to keep the variation of the solvents.

The plot indicates a good linear relationship and the slope is close to unity if one assumes a slip boundary condition.[35] In water, a significant overestimation of the calculated value compared with those in the other solvents was found. This may be attributed to the structure-breaker character of the ammonium ion in the aqueous solution. A similar good correlation and a somewhat exceptional behavior in water are also shown for the perchlorate ion.[12]

4. Discussion

As mentioned in Section 3.3, the hydrodynamic SED model fails to represent the solvent dependence of the rotational relaxation time of the ammonium ion (see Figure 2). This result is reasonably understood by the fact of almost zero hydrody-

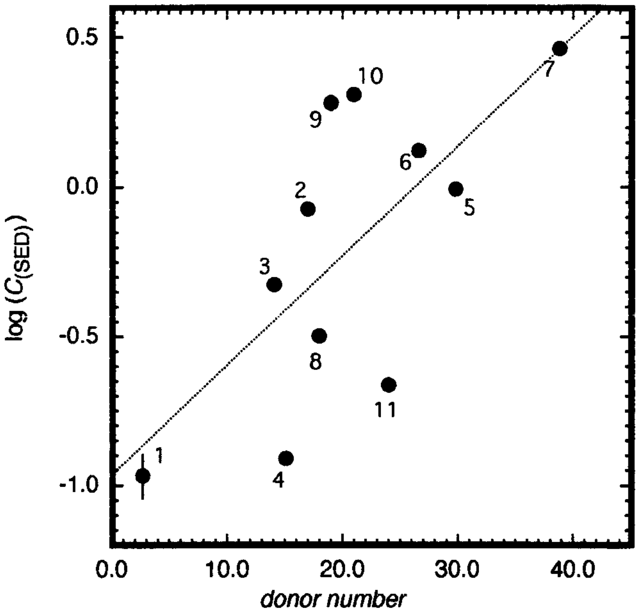

Figure 7. Plot for the logarithms of the C values in the Stokes–Einstein–Debye equation (eq 3) of the ammonium ion versus Gutmann's solvent donor numbers at 298 K. The dotted line indicates the least-squares fitting result assuming a linear relationship. The estimated value was used for the donor number of ethylene glycol (ref 39(b)). The error bars of the data were similar or smaller than the symbols except for that in nitromethane.

namic friction (i.e., the perfect slip hydrodynamic boundary condition) for the rotation of spherical molecules (ions) with a comparable or smaller size than those of the solvents.[32] The inadequacy of the application of the electrohydrodynamic HOF model is also explained in the same manner since the dielectric friction for a rotating charged sphere operates through the hydrodynamic flow in the model.[44] Whereas the observed values of τ_{2r} were much longer than those for the free rotor (~0.2 ps), indicating a contribution of interactions between the fractional charge of the ammonium protons and solvent. Therefore, an application of the AW model should give a better result to represent the solvent dependence than the HOF model since the AW model treats the dielectric friction for the rotating multipole. However, somewhat negative deviations were observed in the plot using the AW model in nitromethane and propylene carbonate compared with those in the other solvents as can be seen in Figure 4. This result underscores the limitations in regarding solvents as dielectric continua since these two solvents have relatively weak donor powers if one considers their dielectric constants.

The logarithms of the rotational relaxation times showed the best linear dependence on Gunman's donor number among the plots attempted in the present study as shown in Figure 5. The hydrodynamic contribution appeared only in the positive deviation of the observed τ_{2r} value in an especially highly viscous solvent of ethylene glycol. One may expect that the higher site–site interactions between positive fractional charge of the protons of the ammonium ion and a negative site of solvent molecule(s) would give the higher hydrodynamic coupling for the ammonium rotation. No prominent correlation was, however, found in the plot of the C values in the SED equation (eq 3) versus the solvent donor numbers as shown in Figure 7. Consequently, the rotational motion of the ammonium ion is simply governed by the energy of the site–site interaction rather than the dynamic properties of the solvents. The rotation of the ammonium ion is similar or even faster than that of the solvent molecules around the ammonium ion, e.g., the rotational relaxation time of water molecule neighboring an ammonium ion is ca. 3 ps,[45] whereas that for the ammonium ion is 1.1 ps. In this extreme, the orientation of the solvent molecules surrounding the ammonium ion is almost frozen during the rotation of the ammonium ion, and the rotation is, thus, achieved in the cavity of the almost frozen solvent cage by the breakdown of the site–site interactions with the solvent molecules. The feature of the ammonium rotation is presumed not to be far from the above extreme case so long as the result of the comparison between the plots in Figures 2–5, and 7. A similar rotational behavior was also found in the solvent dependence of the rotational relaxation times of water. A fairly good correlation was observed between the relaxation time and the chemical shift of water protons as an ensemble-averaged measure of the strength of the local water–solvent interactions.[46]

The effect of such local solvent–solute (ion) interaction on the rotational relaxation time is discussed in a different way in the recent molecular dynamics studies for the rotational relaxation of organic dye molecules,[47] and the MD simulations show that the coupling between the mechanical and dielectric friction caused by changes in the local solvent structures about the solutes plays an important role to determine the feature of the rotational relaxation of the solutes.[47] In this context, inadequacy of the application of the hydrodynamic and dielectric continuum models to the solvent dependence of the rotational relaxation time of the ammonium ion can be attributed to the coupling caused by structural changes of the solvent around the ion, which are driven by the electrostatic field by the positive charge of the ammonium ion or by specific interactions between the ammonium protons and the solvent molecules. This contribution may be particularly important in hydrogen-bonded solvents such as water and alcohols because of the characteristic solvent structures based on the hydrogen-bonding,[48] and the structural variation is closely related to the rotational relaxation time and the feature as shown by the recent MD simulations for water and alcohols.[49]

These behaviors of the solvent dependence of the rotational relaxation times of the ammonium ion are in stark contrast with those for the perchlorate ion; i.e., the solvent viscosity is a good indicator, at least phenomenologically, to represent the solvent dependence of the observed τ_{2r} values of the perchlorate ion as well as the values being much shorter than those of the ammonium ion in almost all solvents used in the present study (see Figure 2). Such a faster rotation and the importance of the hydrodynamic friction for the perchlorate rotation may be attributed to the weakened interaction between the ion and solvent (molecules) due to the lower surface charge density of the perchlorate ion. The difference in the ionic size and the shape between the ammonium ion and the perchlorate ion also contributes to the above different behavior of the solvent dependence. The ionic size of the ammonium ion is smaller and the shape is more spherical (having less roughness on the surface) than those of the perchlorate ion.[20,50] The larger size of the perchlorate ion suffers from the hydrodynamic friction to a higher extent as shown by eq 3b. The uneven surface also increases the contribution of the hydrodynamic friction by partially pushing penetrating solvent molecules aside.[51] Of course, the continuum models predict only a rough trend in the solvent dependence of the perchlorate ion (see Figures 2 and 3), and the deviation from the observed ones shows a correlation to the solvent acceptor numbers.[12] In this context, the perchlorate ion is placed on a border accounting for the effectiveness of an application of the conntinuum models for the rotational motion.

In the comparison of the ionic rotation and the translation, the solvent dependences of the ammonium ion showed clear differences. The linear relationship between the observed friction and those calculated from the electro-hydrodynamic HO model is much better for the ionic translation than rotation, as can be seen from a comparison between Figures 3 and 6. (The rotational friction coefficients are simply proportional to the rotational relaxation times as in eq 3b.) Based on the hydrodynamic or the electrohydrodynamic regime, this result can be understood as follows; under a nearly slip boundary condition, significant translational friction remains due to pressure built up in front of a spherical molecule (ion) ($4\pi R\eta$ in the hydrodynamic model.), whereas the rotational friction approaches zero.[3] Consequently, the contribution of local ion−solvent interactions at the molecular level becomes more noticeable for rotation than for translation. A similar situation also seems to hold in the comparison between the rotation of a spherical and a nonspherical ion (molecule). Successful applications of continuum models to the solvent dependence of the rotational relaxation times of nonspherical molecules, which are determined by recent picosecond fluorescence anisotropy measurements,[52] may be ascribed to the existence of the hydrodynamic friction even at the slip boundary.[53]

5. Conclusions

The rotational relaxation times of the ammonium ion were determined in 11 solvents by measurements of the ^{15}N spin−lattice relaxation times and the NOE factors. The overall trend in the solvent dependence of the obtained τ_{2r} values showed a poor correlation with those predicted on the basis of the SED or the HOF model, that is, the hydrodynamic friction is less important for the ammonium rotation. On the other hand, the observed solvent dependence of the τ_{2r} values showed a better correlation to the logarithms of Guttmann's donor numbers of the solvents. These results indicate that the site−site interaction (the ammonium protons and negative sites of solvent molecules) exceeds the hydrodynamic friction.

Acknowledgment. This work was partially supported by Grants-in-Aid for Scientific Research, No. 12640489 and No. 12023215, for the Ministry of Education, Science and Culture.

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