

Solvent Effect on Rotational Motion of Perchlorate Ion

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The rotational relaxation times of perchlorate ion, τ_{2r} , in 15 solvents and at various temperatures were determined from the measurements of the ^{17}O NMR spin–lattice relaxation times. The obtained τ_{2r} values were much smaller than those predicted from the hydrodynamic model (Stokes–Einstein–Debye, SED, equation). Comparison between the observed solvent dependence of the τ_{2r} value and those predicted by the continuum models, including the SED hydrodynamic model, the Hubbard–Onsager–Felderhof (HOF) electrohydrodynamic model, and the Alavi–Waldeck (AW) dielectric friction model for multipole rotation, demonstrated that solvent viscosity is an expedient indicator for representing the overall trend of the solvent dependence of the rotational relaxation time; the observed τ_{2r} values showed a fractional power dependence on the viscosity (i.e., $\tau_{2r} \propto \eta^\alpha$, where $\alpha \sim 0.25$ and η is the solvent viscosity). Site–site interactions between the perchlorate ion and solvent molecules, however, provided a significant effect on the perchlorate rotation in some solvents with a large imbalance of the electronic donor and acceptor properties (e.g., hexamethylphosphoric triamide). The values for τ_{2r} calculated for alcohols (methanol, ethanol, and *n*-propanol) according to the HOF and the AW models were appreciably overestimated to a greater degree than those in the other solvents, and this result was ascribed to a predominant contribution from the interactions with the hydroxyl groups of the alcohols. The result of the analysis for the solvent dependence of the perchlorate rotation by the electrohydrodynamic model was also compared with that for the perchlorate translation, and the difference in the validity of the continuum models for the ionic rotation and the translation was discussed.

1. Introduction

Ionic rotation and translation are of primary importance to understanding the dynamic features of electrolyte solutions. Studies on ionic translation in solutions, which have been provided by the measurements of ionic conductance, have a long history and have played an important role in constructing the models of ionic solvation (hydration) represented by the Frank–Wen model.¹ Comparisons between the observed translational frictions and those predicted by continuum models (hydrodynamic and dielectric friction models) clarify the validity and limitations of regarding the solvent as a hydrodynamic and/or dielectric continuum in its dynamic aspects.^{2,3}

On the other hand, studies of ionic rotation are less extensive. Systematic studies have been limited only to inorganic ions such as NO_3^- ,^{4–7} CO_3^{2-} ,⁸ XO_4^{n-} ($\text{X} = \text{Cl}, \text{S}, \text{P}$),⁹ and NH_4^+ ,¹⁰ and some metal complex ions.^{11,12} Nevertheless, ionic rotation is an important probe for analyzing the solvation dynamics. The rotational motion of a spherical ion (molecule) does not always require solvent displacement, which is indispensable for ionic (molecular) translation, and therefore may respond to a solvent in some different fashion from translation; for example, under a perfect slip boundary condition in the hydrodynamic regime, the hydrodynamic friction becomes zero for the rotation of a spherical ion (molecule) but is $4\pi R\eta$ for the translation (where R and η are the ionic radius and the solvent viscosity, respectively).¹³ Because of such weak contribution from the hydrodynamic friction to the ionic rotation in the nearly perfect slip limit, the rotational motion is expected to be a sensitive probe for examining the effect of the solvent at the molecular level.

The effect of solvent on the rotational motion of a (spherical) ion also has an important analogy to the rate of ultrafast

intramolecular charge (proton and electron) transfer reactions because the ionic rotation can be regarded as a fractional charge migration within the sphere of the ion if one considers the charge distribution within an ion. The dynamic solvent effect on both the rotational relaxation time and the charge-transfer reaction rate is then reduced to the dynamic response of the solvent polarization to the charge migration in the course of the ionic rotation and of the barrier crossing of the reaction.^{14,15}

From the point of view just presented, systematic experiments on the rotational motions of spherical ions in a wide range of solvents are particularly important, and a test of the continuum (hydrodynamic and dielectric friction) models for the solvent dependence of the rotational relaxation times is expected to provide information on how the molecularity of the solvent affects the ionic rotation. However, such systematic studies only have been done for nitrate ion,¹⁶ but that ion is not spherical and the solvents used were limited to alcohols and a few other solvents.

In the present study, we present the rotational relaxation times of perchlorate ion in 15 solvents, as determined from measurements of ^{17}O NMR spin–lattice relaxation times, and we analyze the results with several hydrodynamic and dielectric friction models.

The perchlorate ion has the following advantages for investigating the solvent effect on the rotation: (i) The perchlorate ion is nearly spherical, which is important to characterizing the rotational motion in comparison with translation. (ii) By choosing a bulky counteranion, the perchlorate ion is soluble in various organic solvents, even those with low dielectric constants. (iii) The ^{17}O spin–lattice relaxation measurement is applicable to determining the rotational relaxation time. Use of a sample that is highly enriched with ^{17}O isotope sample

enables measurement of the spin–lattice relaxation time at very low perchlorate concentrations (see Experimental Section), which is important for separating the solvent effect from ion–ion interactions. (iv) The perchlorate ion has been known as a structure-breaker ion in water. For ionic translation, discrepancy of the observed temperature and pressure dependencies from those predicted by the Hubbard–Onsager electrohydrodynamic model is more pronounced for structure-breaker ions.³ This difference indicates that the rotational motion of the perchlorate ion is, conversely speaking, a suitable probe for measuring the contribution of the ion–solvent interaction at the molecular level and judging the limitations in the application of continuum models.

2. Experimental Section

Materials. The tetra(*n*-propyl)ammonium salt of ¹⁷O-enriched perchlorate was prepared by a previously reported method.⁹ The solution of 6.7 mg of lithium chloride in 0.48 g of ¹⁷O-enriched water (50 atom %, MSD Isotopes, Ltd.) was electrolyzed at 4.8 V with platinum electrodes at 298 K with constant stirring for 15 h. After removal of the water with reduced pressure, an aqueous solution of 0.43 g of tetra(*n*-propyl)ammonium chloride was added into the aqueous solution of the residue. The precipitate of ¹⁷O-enriched tetra(*n*-propyl)ammonium perchlorate that was obtained was filtered and dried under reduced pressure. The yield of the ¹⁷O-enriched tetra(*n*-propyl)ammonium perchlorate was ~90% based on lithium chloride. The isotope concentration of ¹⁷O in the obtained perchlorate was confirmed by the ¹⁷O NMR signal intensity and was ~60%. Lithium chloride and tetra(*n*-propyl)ammonium chloride were purchased from Wako Chemicals, Ltd. (analytical grade) and used without further purification.

¹⁷O NMR Measurement. The ¹⁷O NMR spin–lattice relaxation times, *T*₁, were obtained on a JEOL GSX-270 Fourier transform spectrometer operating at 36.6 MHz (6.35 T) with 5 mm (o.d.) Pyrex tubes. The *T*₁ values for the ¹⁷O nucleus of the perchlorate ion were measured by the usual inversion recovery method with a pulse sequence of (π pulse – Δt – $\pi/2$ pulse)_{*n*}, and the intervals between the sequences were set > 10*T*₁. The *T*₁ values were determined by nonlinear fitting for the signal intensities with > 13 different pulse intervals, Δt . The free induction decay signals were accumulated (e.g., ~2000 times for each Δt for a perchlorate solution of 0.01 mol kg^{−1} concentration). The experimental errors of *T*₁ were within 5%, and the temperature was controlled within ±0.5 °C.

Solvents for NMR measurements were purchased from Wako Chemicals Company, Ltd. (analytical grade), except for hexamethylphosphoric triamide (HMPA) that was from Aldrich Chemical Company, Ltd. The solvents were dried prior to use by standard methods. The measurements were performed without deaerating because of the negligible effect of dissolved oxygen on the observed perchlorate *T*₁ values.^{9,17}

The representative concentration of the perchlorate for the measurements was ~0.01 mol kg^{−1}. To examine the concentration dependence of the *T*₁ values, the measurements were carried out in acetone in the concentration range 0.001–0.2 mol kg^{−1}. The measurements for several dilute solutions (<0.01 mol kg^{−1}) were carried out with a JEOL GSX-400 FT NMR (9.4 T) with 10-mm (o.d.) tubes.

3. Results

3.1. Evaluation of Rotational Relaxation Time. The rotational relaxation times of the perchlorate ion in various solvents were determined by the spin–lattice relaxation times

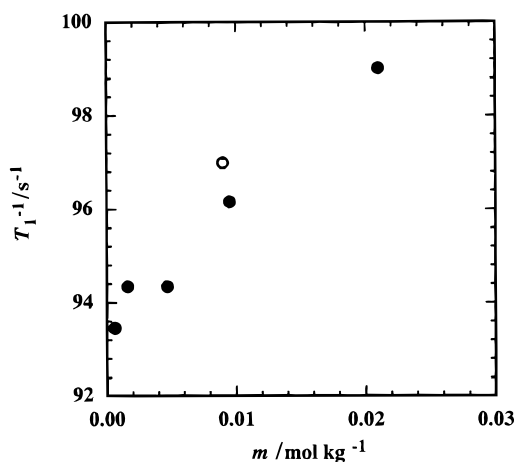


Figure 1. Concentration dependence of the inverse of the ¹⁷O spin–lattice relaxation times of the perchlorate ion, *T*₁^{−1}, in acetone at 298 K. Open and closed circles indicate the values with a GSX 270 (6.3 T) and a GSX 400 (9.4 T) Fourier transform (FT)-NMR spectrometer, respectively.

of the ¹⁷O nucleus of the perchlorate ions. The magnetic relaxation of ¹⁷O (*I* = 5/2) is caused by a so-called quadrupole interaction; that is, the interaction between the electric quadrupole moment of the nucleus and the electric field gradient at the nucleus.^{18,19} The ¹⁷O spin–lattice relaxation time, *T*₁, at the extreme narrowing limit is then expressed by eq 1:¹⁹

$$T_1^{-1} = \frac{3}{40} \frac{2I + 3}{I^2(2I - 1)} \left(1 + \frac{\alpha^2}{3} \right) \left(\frac{e^2 Q q}{\hbar} \right)^2 \tau_c \quad (1)$$

where *eQ*, *eq*, and α represent the quadrupole moment of the ¹⁷O nucleus (*Q* = −0.0265 × 10^{−24} cm²),²⁰ the main axis component of the electric field gradient (efg) at the ¹⁷O nucleus, and the asymmetry parameter, respectively, and τ_c is the correlation time of the fluctuation of the field gradient. In the present case, the τ_c value corresponds to the rotational relaxation time of the perchlorate ion associated with the second rank spherical harmonics, τ_{2r} .^{9,17}

The values of *eq* and α [i.e., *eq* = 2.37 au and α = 0 (1 au = 9.7175 × 10²¹ V m^{−2})], which were previously obtained by an ab initio MO calculation for an isolated perchlorate ion,⁹ were used for the present study. The effect of solvent molecules surrounding the perchlorate ion on the *eq* (and α) values was assumed to be negligible as previously reported.^{9,21} Thus, the reorientational relaxation times of the perchlorate ion in various solvents and at various temperatures were determined from the observed *T*₁ values and the aforementioned *eq* value according to eq 1.

The effect of ion–ion interaction on the rotational relaxation time was examined as follows. Figure 1 shows the dependence of the *T*₁^{−1} values of perchlorate ¹⁷O, which are proportional to τ_{2r} , on the concentration of the tetrapropylammonium perchlorate in acetone. The *T*₁^{−1} values (i.e., the τ_{2r} values), decrease almost linearly with decreasing concentration below 0.02 mol/kg as predicted by Ibuki et al.²² However, the effect of the counter-cation on the τ_{2r} values below the perchlorate salt concentration of 0.01 mol kg^{−1} was not beyond 5% of the τ_{2r} value extrapolated to the infinite dilution. The effect of the counter-cation on τ_{2r} is expected to be 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 0.01 mol kg^{−1} were regarded as those at infinite dilution in all the solvents, considering the experimental error in the *T*₁ measurements.

TABLE 1: The Rotational Relaxation Times of the Perchlorate Ion in Various Solvents and Their Physical Properties at 298 K

	solvent	$\tau_{2r} (\times 10^{-13})$, s	C^a	viscosity, cP	ϵ_0^b	ϵ_∞^b	$\tau_D \{ \times 10^{-12} \}$, s ^b
1.	water	6.16	0.049	0.890 ^c	78.3 ^e	5.2 ^e	8.2 ^e
2.	acetonitrile	5.06	0.104	0.345 ^c	37.5 ^f	2 ^f	3.3 ^f
3.	acetone	4.70	0.106	0.316 ^c	21 ^g	3.3 ^g	2 ^g
4.	nitromethane	5.87	0.067	0.62 ^d	36 ^g	3.9 ^g	2 ^g
5.	<i>N,N</i> -dimethylformamide (DMF)	5.41	0.048	0.796 ^c	36.7 ^f	4.5 ^f	11.0 ^f
6.	dimethylsulfoxide (DMSO)	6.51	0.024	1.96 ^c	46.7 ^f	5.7 ^f	19.5 ^f
7.	propylene carbonate	7.34	0.023	2.53 ^c	65 ^f	4.1 ^f	43 ^f
8.	tetramethylurea	8.12	0.037	1.40 ^d	23.1 ^f	4.5 ^f	31 ^f
9.	hexamethylphosphoric triamide (HMPA)	7.01	0.0154	3.23 ^d	29.6 ^g	3.3 ^g	80 ^g
10.	benzonitrile	8.43	0.050	1.22 ^c	25.6 ^f	3.9 ^f	38 ^f
11.	nitrobenzene	9.36	0.036	1.85 ^c	35.7 ^g	4.1 ^g	45.6 ^g
12.	methanol	5.85	0.076	0.545 ^c	32.7 ^f	5.6 ^f	48 ^f
13.	ethanol	6.86	0.045	1.09 ^c	32.5 ^{h,i}	2.8 ^{h,i}	51.5 (0.89), 7.1 (0.04), 1.1 (0.07) ^{h,i}
14.	<i>n</i> -propanol	8.22	0.028	2.08 ^c	24.5 ^f	4.2 ^f	130 ^f
15.	ethylene glycol	13.9	0.0061	16.17 ^c	24.3 ^{h,j}	2.7 ^{h,j}	163 (0.93), 8.9 (0.04), 1.8 (0.05) ^{h,j}
					20.4 ^f	2.2 ^f	340 ^f
					27.4 ^{h,i}	2.5 ^{h,i}	390 (0.93), 21.9 (0.03), 2.1 (0.04) ^{h,i}
					37.9 ^k	2.3 ^k	105 ^k
					37.9 ^{k,l}	2.0 ^{k,l}	124 (0.93), 12.2 (0.07) ^{k,l}

^a $C = \tau_{2r}(\text{obs}) / ((4/3)\pi R^3 \eta / k_B T)$; see eq 2b. ^b Assuming single dielectric relaxation unless otherwise stated. ^c Viswanath, D. S.; Natarajan, G. *Viscosity of Liquids*; Hemisphere: New York, 1989. ^d Ridick, A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents, Physical Properties and Methods of Purification*; Wiley: New York, 1986. ^e Evans, D. F.; Tomimaga, T.; Hubbard, J. B.; Wolynes, P. G. *J. Phys. Chem.* **1979**, *83*, 2669. ^f McManis, G. E.; Golovin, M. N.; Weaver, M. J. *J. Phys. Chem.* **1986**, *90*, 6563. ^g Nielson, R. M.; McManis, G. E.; Golovin, M. N.; Weaver, M. J. *J. Phys. Chem.* **1988**, *92*, 3441. ^h Triple relaxation is assumed; the values in the parentheses are amplitude factors for the corresponding relaxations. ⁱ Maroncelli, M. J. *Mol. Liq.* **1993**, *57*, 1. ^j Barthel, J.; Bachhuber, K.; Hetzenauer, H. *Chem. Phys. Lett.* **1990**, *165*, 369. ^k McManis, G. E.; Weaver, M. J. *J. Chem. Phys.* **1989**, *90*, 912. ^l Double relaxation is assumed; the values in the parentheses are amplitude factors for the corresponding relaxations.

3.2. Analysis of Rotational Relaxation Times. The rotational relaxation times obtained in various solvents at 298 K are listed in Table 1 together with some solvent properties. The solvent dependence of the rotational relaxation times was compared with the solvent dependence of values predicted by the following several models.

Hydrodynamic Model. The Stokes–Einstein–Debye (SED) equation is one of the simplest representations for molecular (ionic) rotation, where the ion (molecule) and 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).^{23,24} The hydrodynamic friction, $\zeta_r(\text{SED})$, and the rotational relaxation time, τ_{2r} , for a rotating sphere with the radius R in a solvent with viscosity η are then represented by:²³

$$\zeta_r(\text{SED}) = C(8\pi R^3)\eta \quad (2a)$$

and

$$\tau_{2r}(\text{SED}) = \frac{\zeta_r(\text{SED})}{6k_B T} = C \left(\frac{4}{3}\pi R^3 \right) \eta / k_B T \quad (2b)$$

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).

A linear relationship between rotational relaxation time and viscosity with a zero-viscosity intercept has often been found for spherical or nearly spherical molecules, and the intercept has been discussed in relation to the inertial character of the rotational motion.^{23,25} However, in the plot of the observed τ_{2r} value against solvent viscosity (Figure 2), any meaningful zero-intercept cannot be determined because the plot steeply curves downward with decreasing viscosity. [The solvent dependence of the τ_{2r} values observed were roughly fitted by a fractional exponent of solvent viscosity; i.e., $\tau_{2r} \propto \eta^\alpha$ ($0 < \alpha < 1$), as

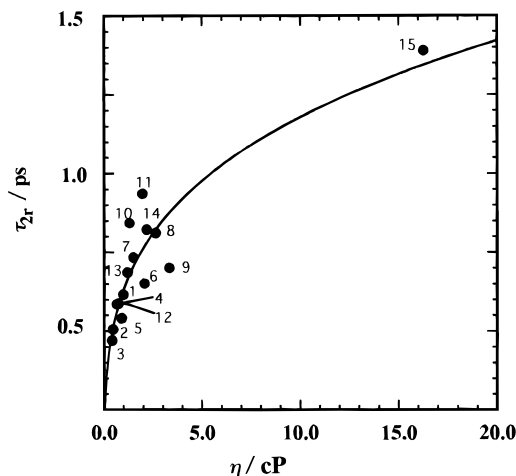


Figure 2. Viscosity dependence of the observed τ_{2r} values in various solvents at 298 K. The solvents used for the measurements are as follows: (1) water; (2) acetonitrile; (3) acetone; (4) nitromethane; (5) *N,N*-dimethylformamide (DMF); (6) dimethylsulfoxide (DMSO); (7) propylene carbonate; (8) tetramethylurea; (9) hexamethylphosphoric triamide (HMPA); (10) benzonitrile; (11) nitrobenzene; (12) methanol; (13) ethanol; (14) *n*-propanol; (15) ethylene glycol. The solid line in the figure indicates the least-squares fitting result (i.e., $\tau_{2r} = 1.18 \times 10^{-12} \times \eta^{0.25}$).

shown by the solid line in Figure 2.²⁶) Because of this situation, we do not consider the zero-intercept in the following discussion.

Values of C for the various solvents at 298 K were calculated from the ratio of the observed τ_{2r} values to the values calculated by eq 2b, assuming the stick boundary condition, and are listed in Table 1. (The ionic radius is taken to be 2.4 Å.) The C values obtained in this manner ranged from 0.006 to 0.1.²⁷ In Figure 3, the logarithms of the observed τ_{2r} values in various solvents at 298 K are plotted against those calculated according to eq 2b, assuming $C = 1$. Although considerable scatter is displayed in the plot, a rough linear relationship can be seen between the observed and the calculated values, with a slope of ~ 0.25 . Similar behavior is also observed in a log plot of

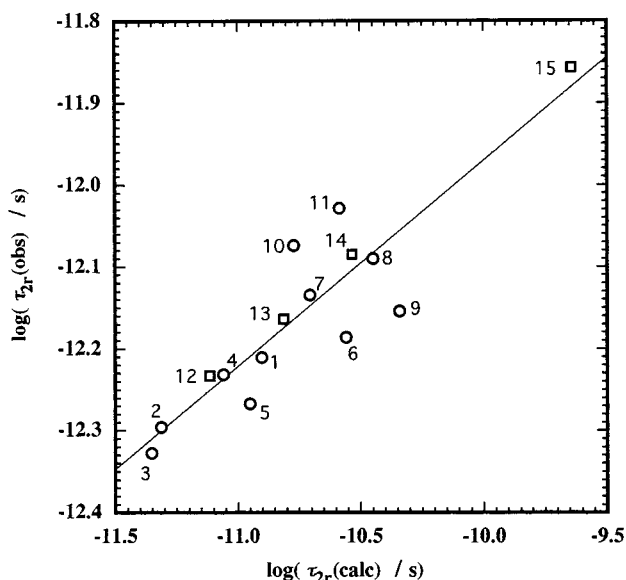


Figure 3. Logarithm plot of the observed τ_{2r} values versus those calculated by the Stokes–Einstein–Debye equation assuming the stick hydrodynamic boundary condition ($C = 1$ in eq 2) at 298 K. The solvents used for the measurements are as follows: (1) water; (2) acetonitrile; (3) acetone; (4) nitromethane; (5) *N,N*-dimethylformamide (DMF); (6) dimethylsulfoxide (DMSO); (7) propylene carbonate; (8) tetramethylurea; (9) hexamethylphosphoric triamide (HMPA); (10) benzonitrile; (11) nitrobenzene; (12) methanol; (13) ethanol; (14) *n*-propanol; (15) ethylene glycol. The solid line in the figure indicates the least-squares fitting result assuming a linear relationship between the observed and the calculated $\log \tau_{2r}$ values with a slope of 0.25. The ionic radius of the perchlorate ion is assumed to be 2.4 Å for the calculation.

the temperature dependence of the friction coefficients determined from the observed τ_{2r} values and those calculated by the SED equation (eq 2a) for each solvent, as shown in Figure 4. This plot shows an approximately linear relationship for the temperature dependence in each solvent, and the slope was ~ 0.4 for most solvents in the present study.

Hubbard–Onsager–Felderhof (HOF) Electrohydrodynamic Model. In the SED model, the interactions between the ionic charge and the dielectric properties of the solvent are disregarded. The effect of the ionic charge on the friction of ionic rotation is treated by Felderhof,²⁸ where coupling of the hydrodynamic and the dielectric effects is taken into account according to Hubbard–Onsager electrohydrodynamic model.²⁹ The reorientational relaxation time for a spherical ion is then represented by:²⁸

$$\tau_{2r}(\text{HOF}) = \left(\frac{4}{3} \pi R^3 \right) \left(\frac{\eta}{k_B T} \right) \left(\frac{1}{1 - C J(u)} \right) \quad (3a)$$

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

$$u = R_{\text{HO}}/R \quad (3c)$$

where C is the parameter for the hydrodynamic boundary condition whose meaning is the same as that in the SED model (eq 2). The Hubbard–Onsager radius, R_{HO} is given by:

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

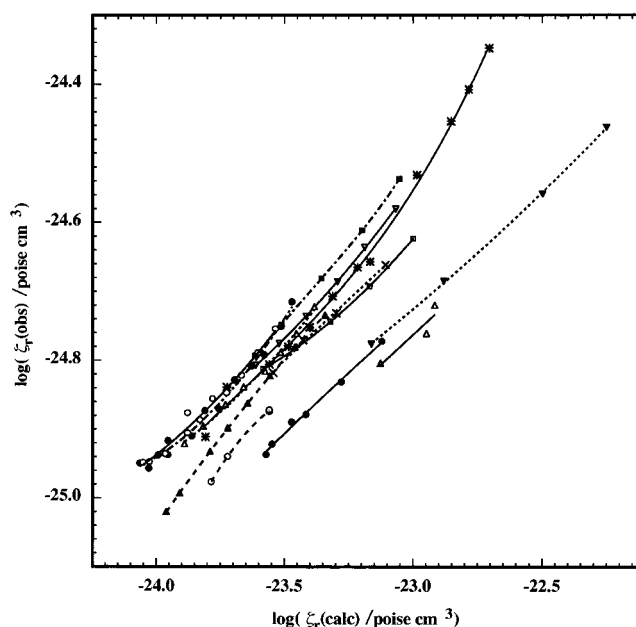


Figure 4. Plots of the logarithms of the observed temperature dependences of the friction coefficients of the perchlorate rotations, $\zeta_r(\text{obs})$, versus those calculated by the Stokes–Einstein–Debye equation, $\zeta_r(\text{calc})$, assuming the stick boundary in various solvents. Key: (—▲—) water; (—○—) acetonitrile; (—●—) acetone; (···△···) nitromethane; (—○—) *N,N*-dimethylformamide (DMF); (—●—) dimethylsulfoxide (DMSO); (—△—) hexamethylphosphoric triamide (HMPA); (—■—) benzonitrile; (—▽—) nitrobenzene; (—*—) methanol; (···×···) ethanol; (—□—) *n*-propanol; (···▼···) ethylene glycol.

where z is the ionic charge and ϵ_0 , ϵ_∞ , and τ_D are the static and high-frequency dielectric constants and the dielectric relaxation time of the solvent, respectively.

Figure 5 shows a logarithm plot of the observed τ_{2r} values in various solvents at 298 K versus those calculated according to the HOF model. This plot shows a rough trend similar to that in Figure 3, except for alcohols. The similarity is due to the close similarity in the τ_{2r} values calculated by the SED and HOF models, except in the case of alcohols.

Dielectric Friction for a Rotating Multipole. There is a $-0.44 e$ fractional charge on each of the four oxygen atoms of the perchlorate ion.⁹ However, in the electrohydrodynamic HOF model as well as the hydrodynamic SED model, such a charge distribution within the ion is disregarded. The dielectric friction for the rotation of the perchlorate ion as an octapole with fractional charges on the oxygen atoms can be calculated with an equation presented by Alavi and Waldeck,³⁰ which is an extension of the dielectric friction for a rotating dipole given by Nee and Zwanzig.³¹ Thus, the calculated τ_{2r} is represented by:^{30b}

$$\tau_{2r}(\text{AW}) = \left(\frac{1}{6k_B T} \right) \left(\frac{2\tau_D}{a} \right) \sum_{j=1}^N \sum_{i=1}^N \sum_{L=1}^{\infty} \sum_{M=1}^L \left(\frac{2L+1}{L+1} \right) \times \left[\frac{\epsilon_0 - \epsilon_\infty}{\left(\epsilon_0 + \epsilon_\infty \frac{L}{L+1} \right)^2} \right] \frac{(L-M)!}{(L+M)!} \times M^3 q_i q_j \left(\frac{r_i}{a} \right)^L \left(\frac{r_j}{a} \right)^L P_L^M(\cos \theta_i) P_L^M(\cos \theta_j) \cos M\phi_{ij} \quad (5)$$

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

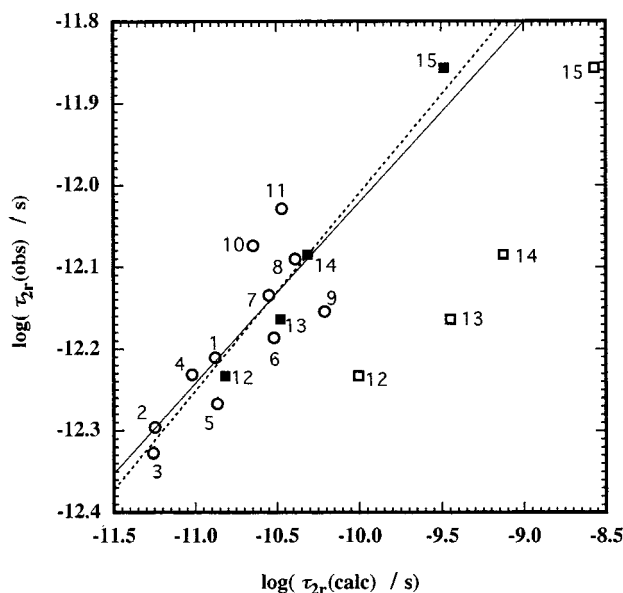


Figure 5. Logarithm plot of the observed τ_{2r} values versus those calculated by the Hubbard–Onsager–Felderhof model assuming the stick hydrodynamic boundary condition at 298 K. Open and closed square symbols correspond to the calculated values in alcohols, with the classical Debye dielectric relaxation times and with the two shorter (for methanol, ethanol, and *n*-propanol) or the shortest (for ethylene glycol) relaxation times assuming the multiple relaxations, respectively (see text and Table 1). The number assigned to each solvent is the same as that in Figure 3. The solid line in the figure indicates the least-squares fitting result assuming a linear relationship between the observed and the calculated $\log \tau_{2r}$ values in the solvents other than alcohols (open circles), with a slope of 0.22, and the broken line shows the results in solvents including alcohols, taking into account the faster non-Debye relaxations (open circles and closed squares), with a slope of 0.24. The ionic radius is assumed to be 2.4 Å for the calculation.

Figure 6 shows a plot of the logarithms of the observed τ_{2r} values in various solvents at 298 K against those calculated according to the Alavi–Waldeck (AW) model in eq 5. Although the observed and calculated τ_{2r} values show a weak positive correlation, the scatter is relatively large. Like in the plot for the HOF model shown in Figure 5, the calculated values for alcohols were more appreciably overestimated than those in the other solvents.

4. Discussion

The rotational relaxation times of sulfate and phosphate ions, which have ionic radii comparable to that of the perchlorate ion but higher ionic charges, are longer than those of the perchlorate ion by a factor of 10 or more in water at 25 °C.⁹ This retardation in the rotation of the higher charged ion can be attributed to interaction between the ionic charge and the solvent as predicted, for example, by the HOF electrohydrodynamic model.³² Such an effect of ionic charge on the rotational motion is also demonstrated in the comparison between τ_{2r} values of nitrate and carbonate ions in water.⁸

The SED equation is conceptually valid when the size of a molecule (ion) is large enough for the solvent to be regarded as a continuum.^{23,24} In fact, the rotational relaxation times of several spherical metal complex ions with relatively large ionic radii are well represented by the SED equation with a stick boundary (i.e., $C = 1$ in eq 2b).^{11,12} (The effect of the ionic charges is negligibly small because of the small surface charge densities.) On the other hand, the phenomenological hydrodynamic boundary approaches slip ($C \ll 1$) when the size of a solute molecule is comparable with the solvent molecules, as

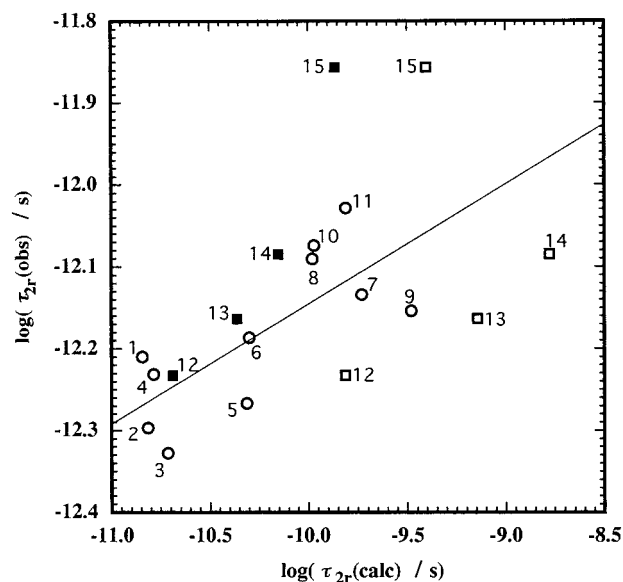


Figure 6. Logarithm plot of the observed τ_{2r} values versus those calculated by the Alavi–Waldeck model at 298 K. Open and closed square symbols correspond to the calculated values in alcohols with the classical Debye dielectric relaxation times and with the two shorter (for methanol, ethanol, and *n*-propanol) or the shortest (for ethylene glycol) relaxation times assuming the multiple relaxations, respectively (see text and Table 1). The number assigned to each solvent is the same as that in Figure 3. The solid line in the figure indicates the least-squares fitting result assuming a linear relationship between the observed and the calculated $\log \tau_{2r}$ values in the solvents other than alcohols (open circles), with a slope of 0.15. The ionic radius, the Cl–O bond length, and the fractional charge on each oxygen atom are assumed to be 2.4 Å, 1.46 Å, and $-0.44 e$, respectively.

reported by Pecora et al.³³ Thus, the observation of the C values much smaller than unity for the rotational motion of the perchlorate ion (Table 1) can be attributed to the comparable size of the ion and solvent molecules and the minor effect of the ionic charge on the rotational friction as shown by the calculation based on the electrohydrodynamic (HOF) model, considering the ionic radius (2.4 Å) and the univalent charge (see Section 3.2).

The overall trend of the observed τ_{2r} values in Figure 3 can be described by a η^α dependence ($\alpha \sim 0.25$); that is, the C values decreased with an increase in solvent viscosities. Similar behavior was also found in the application of the HOF model; the logarithms of the observed and the calculated τ_{2r} values showed a roughly linear relationship, with a slope of 0.23 except for those in alcohols (see Figure 4). Such a fractional power ($0 < \alpha < 1$) dependence of friction on viscosity has been found not only in molecular rotations where viscosity was varied over a wide range by variation of solvent and by temperature and pressure tunings,^{34,35} but also in the barrier crossing dynamics for ultrafast chemical reactions; for examples, large-amplitude isomerizations for the hydrodynamic friction^{15,36} and electron-transfer reactions for the dielectric friction.^{15,37} This phenomenon can be understood in terms of a frequency dependent friction; that is, the effective friction decreases when solvent relaxation is much slower than the observing dynamics.^{38,39} In the case of the perchlorate ion, the time scale of the rotation is much shorter than the solvent relaxation times in highly viscous solvents (e.g., in ethylene glycol), where the observed τ_{2r} values are >1 order of magnitude shorter than the solvent relaxation time at room temperature. In such a case the effective friction for the perchlorate rotation will decrease; that is, the apparent C value decreases.

The overestimation in the τ_{2r} values by the HOF model was much greater in alcohols (methanol, ethanol, and *n*-propanol) than in the other solvents,⁴⁰ and that by the AW model was even more noticeable (see the open squares in Figures 5 and 6), whereas such a trend was not found in the SED model (see Figure 3). This characteristic behavior in the alcohols indicates that the perchlorate rotation does not sense the appreciable dielectric friction predicted by the abnormally long dielectric relaxation times (Debye relaxation times), τ_D , of the alcohols compared with those of the other solvents, as shown in Table 1, because of the much shorter time scale of the rotational motion of the perchlorate ion relative to the dielectric relaxation times of the alcohols.³⁶ Consequently, the rotational relaxation times may be predominantly controlled by local ion–solvent interactions (i.e., those with the OH groups of the alcohols). Then, an effective dielectric friction for the perchlorate rotation originating from the rotations of the alcohol molecule or its OH group based on the HOF or the AW model can be estimated from the dielectric relaxation times assigned to these local motions of the alcohols, which have been observed in recent microwave experiments and are one or two orders shorter than the dielectric relaxation times of the major component or the classical Debye ones^{41,42} (see Table 1). The τ_{2r} values thus calculated are plotted as closed square symbols against those observed in Figures 5 and 6. The behavior in alcohols approaches the trend of the other solvents. Such a predominant effect of the components with the shorter dielectric relaxation times of alcohols has also been found in the solvent dielectric friction for barrier crossing dynamics in ultrafast electron-transfer reactions.⁴³

For the solvents other than the alcohols, small but meaningful deviations from the linear relation in the logarithm plots for the SED and the HOF models (Figures 3 and 5) can be seen in several solvents; that is, the extent of overestimation by the SED equation for τ_{2r} is larger in HMPA, DMSO, and probably in DMF and somewhat less in benzonitrile and nitrobenzene than in the other solvents. This result suggests a problem with disregarding the structure of the perchlorate ion (fractional negative charge on the oxygen atoms) and/or solvent molecular for these solvents. The former effect is expected to be introduced by application of the AW model.³⁰ However, the plot in Figure 6 for this model showed even less correlation between the observed and calculated τ_{2r} values than those found in Figures 3 and 5. This fact may be ascribed to the following reasons: (i) the AW model disregards the hydrodynamic friction. The large leftward shift in the point for highly viscous ethylene glycol in Figure 6 indicates the importance of the hydrodynamic friction. (ii) When the dimension of the charge distribution of a rotating molecule (or ion) is comparable or smaller than that of a solvent molecule, regarding the solvent as a dielectric continuum gives rise to a conflict.^{30b} (The ionic size of the perchlorate ion is comparable or even smaller than the size of almost all of the solvents used in the present study.)

Thus, the scatter in the SED or the HOF plot as shown in Figures 3 and 5 (e.g., in HMPA), is not fully settled so far as one regards the solvent as a hydrodynamic and/or dielectric continuum, and local ion–solvent interactions should be taken into account to consider the behavior of solvent dependence of τ_{2r} particularly in some solvents, (e.g., HMPA, DMSO, and DMF) that showed significant discrepancy from the correlation in the other solvents. These solvents can be distinguished from the other solvents by a considerable imbalance in the strength of their interactions with an anion versus a cation. For example, HMPA, DMSO, and DMF have very high Gutmann donor

numbers, but their acceptor numbers are relatively small.⁴⁴ This relationship may suggest a smaller effective friction for the rotation resulting from interactions between the negative perchlorate oxygens and the solvents than would be predicted by treating the solvents as hydrodynamic and/or dielectric continua because the viscosities and the dielectric properties, particularly dielectric relaxation times, of solvents largely depend on the polarities of solvent molecules as a whole. Consequently, the hydrodynamic (SED) and electrohydrodynamic (HOF) models show a larger extent of the overestimation of the rotational relaxation times in these solvents than in the other solvents. Small leftward shifts for benzonitrile and nitrobenzene in the plots in Figures 3 and 5 may be similarly explained. Both of the solvents have a relatively large nonpolar phenyl group, and local interactions between the perchlorate oxygens and the nitrile or the nitro group of the solvents, which have considerably large acceptor powers (numbers), may largely retard the rotational motion.

Of course, such a site–site interaction also contributes to the perchlorate rotation in other solvents, whose electron donor and acceptor powers are not so imbalanced. In these solvents, an increase in the acceptor power (i.e., an increase in the solvent polarity), enhances the solvent–perchlorate interaction, and the interaction seems to retard the perchlorate rotation. However, at same time, this increase in the solvent polarity increases the solvent viscosity and the dielectric relaxation time, which lead to an increase in the predicted rotational friction by the hydrodynamic and the dielectric continuum model (see eqs 2, 3, and 4). Consequently, the solvent viscosity becomes an expedient indicator, at least phenomenologically, for representing the solvent dependence of the rotational relaxation times.

Finally, a comparison of the validity of the continuum models for the solvent dependence of the rotational motion with that of the translational motion of the perchlorate ion is worth noting, particularly for the Hubbard–Onsager (HO) electrohydrodynamic model. Figure 7 shows a logarithm plot of the calculated friction coefficients of the translational motion of the perchlorate ion, $\zeta_t(\text{HO})$, at 298 K based on the HO electrohydrodynamic model according to an expression given in the literature^{3,45} versus those obtained with the observed limiting ionic conductance by the following relation;

$$\zeta_t(\text{obs}) = eF/\lambda_o \quad (6)$$

where F and λ_o indicate the Faraday constant and the ionic limiting conductance, respectively. The plot indicates a good linear relationship and the slope is close to unity, except for alcohols, when the classical Debye dielectric relaxation times, τ_D , are used for the calculations. (See square open symbols in Figure 7).⁴⁶ However, if one or two faster but minor relaxation components given in Table 1 are considered for the translational friction in alcohols, as was done in the HOF analysis of the rotational motion shown by the closed squares in Figure 5, then the calculated values for the alcohols in the plot shift to the left and on to the line with the other solvents (see closed squares in Figure 7). In water, a slightly larger extent of overestimation of the calculated value compared with those in the other solvents was indicated. This result may be attributed to the structure-breaker character of the perchlorate ion in the aqueous solution.

However, in general, the linear relationship between the observed values and those calculated from electrohydrodynamic friction models is much better for the ionic translation than for rotation, as can be seen from a comparison between Figures 5 and 7. (The rotational friction coefficients are simply proportional to the rotational relaxation times as in eq 2b.)

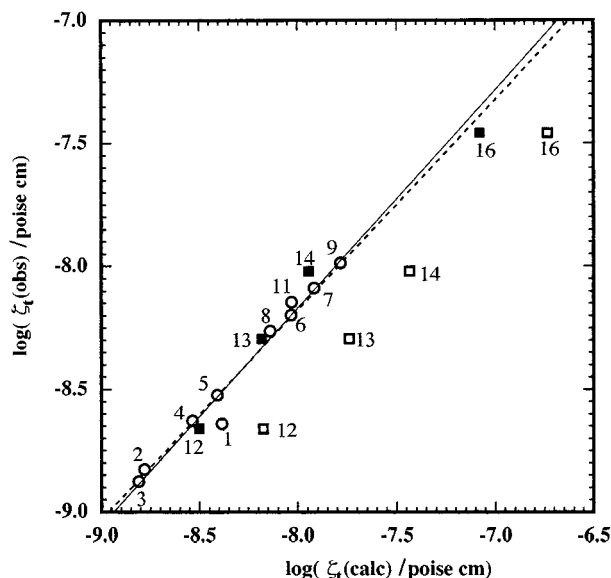


Figure 7. Logarithm plot of the translational friction coefficients determined with the limiting values of the electric conductance of the perchlorate ion, $\zeta_t(\text{obs})$, versus those calculated by the Hubbard–Onsager model in various solvents at 298 K assuming the stick boundary, $\zeta_t(\text{calc})$. Open and closed square symbols correspond to the calculated values in alcohols with the classical Debye dielectric relaxation times and with the two shorter (for methanol, ethanol, and *n*-propanol) or the shortest (for ethylene glycol) relaxation times assuming the multiple relaxations, respectively (see text and Table 1). The number assigned to each solvent is the same as that in Figure 3. The solid line in the figure indicates the least-squares fitting result assuming a linear relationship between the observed and the calculated $\log \tau_{2r}$ values in the solvents other than alcohols (open circles), with a slope of 0.84, and the broken line shows the result in solvents including alcohols, taking into account the faster non-Debye relaxations (open circles and closed squares), with a slope of 0.86. The value of the conductance in water is taken from Robinson, R. A.; Stokes, R. H. *Electrolyte Solutions*; Butterworths: London, 1959; pp 465; that for acetonitrile is from Barthel, J. J. *Solution. Chem.* **1990**, *19*, 321; and those for all other solutions are from Krumgalz, B. S. *J. Chem. Soc., Faraday Trans. 1* **1983**, *79*, 571.

Based on the hydrodynamic or the electrohydrodynamic regime, this result can be understood as follows; under nearly slip boundary, significant translational friction remains due to pressure built up in front of a spherical molecule or ion ($4\pi R\eta$ in the hydrodynamic model⁴⁷), whereas the rotational friction approaches to zero. 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 given by recent picosecond fluorescence anisotropy measurements,⁴⁸ may be ascribed to an existence of the hydrodynamic friction even at slip boundary.⁴⁹

5. Conclusions

The rotational relaxation times of the perchlorate ion were determined in 15 solvents and at various temperatures by the measurements of the ^{17}O spin–lattice relaxation times. The overall trend of the solvent dependence of the τ_{2r} values obtained showed a fractional power dependence on those predicted based on the SED or the HOF model; that is, these continuum models are expedient, at least phenomenologically, for representing the solvent dependence of the perchlorate rotation. Nevertheless,

the predominant contribution of the hydrodynamic or the dielectric friction cannot be expected in the case of the spherical perchlorate ion whose size is comparable to that of solvent. These results indicate that an increase in the site–site interaction responsible for the rotational motion is roughly balanced with the solvent viscosity or the dielectric relaxation time unless electron donor and acceptor powers of solvent are appreciably imbalanced, as for HMPA solvent where significant deviation is found in the trend for the other solvents in the plots of the observed τ_{2r} values against those calculated on the basis of the SED or the HOF model.

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