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Pronounced Dielectric Relaxation Behavior of a Small Ionic Species, *p*-Toluenesulfonate, in Aqueous Solution

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Aqueous solutions of a small size electrolyte, sodium *p*-toluenesulfonate (Na*p*TS), were examined for dielectric relaxation behavior. Dissociated *p*TS$^-$ shows pronounced dielectric relaxation behavior in the aqueous solutions well-described with a Debye-type relaxation function. The value of the dielectric relaxation time is much longer than that of water molecules and is very close to the rotational relaxation time determined from the value of a spin−lattice relaxation time (T_1, ^{1}H NMR). This means that *p*TS$^-$ keeps significantly large dipole moment (μ) and its rotational relaxation mode is detected by the dielectric relaxation measurements. Moreover, the concentration dependence of dielectric relaxation data suggests that 2−3.5 water molecules are tightly hydrated to *p*TS$^-$ in aqueous solution. We also carried out ab initio quantum chemical calculations to obtain the optimized geometries of individual *p*TS$^-$, *p*TS$^-$ dihydrate, and *p*TS$^-$ trihydrate. The magnitudes of μ evaluated to be 7.3, 6.1, and 6.2 D, respectively, at the optimized geometries are significantly large and are crucial evidence that *p*TS$^-$ keeps large μ in aqueous solution.

Introduction

In general, dissociated small and simple ionic species such as sodium (Na$^+$), potassium (K$^+$), bromide (Br$^-$), and chloride (Cl$^-$) ions in aqueous solution behave as point charges, which only carry electric charges but do not exhibit dielectric responses.[1] Moreover, from the viewpoint of theoretical consideration, the vector of dipole moment for ionic species such as Na$^+$ is not determined uniquely according to a standard definition of the dipole moment. The standard definition of the dipole moment vector of a particle is given by eq 1,[2]

$$\mu = \int_{\partial v} \mathbf{r}\rho_{\mathrm{e}(\mathbf{r})}\, \mathrm{d}^3\mathbf{r} \qquad (1)$$

$$\int_{\partial v} \rho_{\mathrm{e}(\mathbf{r})}\, \mathrm{d}^3\mathbf{r} = 0 \qquad (2)$$

where $\mathbf{r}$, $\rho_{\mathrm{e}(\mathbf{r})}$, and ∂v represent a position vector, electric charge density at $\mathbf{r}$, and the volume of the particle, respectively. The value of μ is uniquely determined by eq 1 only for electrically neutral species satisfying eq 2. However, in the case of an ionic species that does not satisfy eq 2, the value of μ depends on selection of the origin of a used coordinate system. Now, we consider one of the simplest situations for an ionic species depicted in Figure 1. A positive charge of $\delta q + q$ is located at $\mathbf{r}_1$, while a negative charge of $-q$ is located at $\mathbf{r}_2$; q is a positive value. Then, μ is calculated to be $q(\mathbf{r}_1 - \mathbf{r}_2) + \delta q\mathbf{r}_1$ by use of eq 1. The former term of $q(\mathbf{r}_1 - \mathbf{r}_2) = q\mathbf{r}_{12}$ is determined uniquely, while the latter term of $\delta q\mathbf{r}_1$ depends on the value of $\mathbf{r}_1$ according to eq 1. Therefore, people had not thought that small ionic species have dipolar characteristics for a long time.

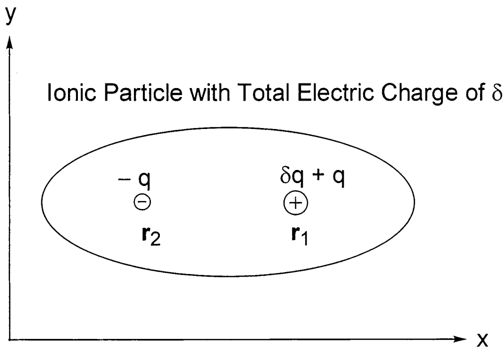

Figure 1. Schematic representation of an ionic particle bearing an asymmetric electric charge distribution.

Several years ago, Kaatze et al. investigated dielectric relaxation behavior of aqueous solutions of multivalent electrolytes such as zinc chloride (ZnCl$_2$),[3] aluminum sulfate (Al$_2$(SO$_4$)$_3$), scandium sulfate (Sc$_2$(SO$_4$)$_3$), and indium sulfate (In$_2$(SO$_4$)$_3$).[4] They found that an ionic species of (ZnCl)$^+$ presents in aqueous ZnCl$_2$ solutions and shows marked dielectric relaxation behavior, and they concluded that the ionic species not only carries electric charges but also possesses a permanent dipole moment.[3] Other types of ionic species bearing dipole moments have been also found in several aqueous solutions of asymmetric multivalent electrolytes.[4−8] These findings require another definition for μ than that in eq 1, which must be valid not only for electrically neutral dipolar species but also for ionic dipolar species.

The first derivative of the formation energy (W) of an electrically neutral molecular species with respect of the electric field ($\mathbf{E}$) applied to the molecule in each direction (x, y, and z) is another definition of μ as given by eq 3.[9]

$$\mu j = -\frac{\partial W}{\partial \mathbf{E}j} \qquad (j = x, y, \text{and } z) \qquad (3)$$

Here, we consider the application of eq 3 to ionic dipolar species. The value of W for the simplest ionic particle in Figure 1 is

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calculated as follows. First, a standard condition is defined as a point electric charge of δq is carried to $\mathbf{r}_1$ from the original position of $\mathbf{r}_0$ under a stationary electric field of $\mathbf{E}$. Then, the electric charge of $-q$ is moved from $\mathbf{r}_1$ to $\mathbf{r}_2$ under the applied electric field of $\mathbf{E}$. Consequently, the ionic particle generates as shown in Figure 1 under $\mathbf{E}$, and the value of W in the procedure is calculated to be eq 4,

$$W = -\delta q(\mathbf{r}_1 - \mathbf{r}_0)\mathbf{E} - q(\mathbf{r}_1 - \mathbf{r}_2)\mathbf{E} - \frac{(\delta + 1)q^2}{4\pi\epsilon_v|\mathbf{r}_2 - \mathbf{r}_1|} \quad (4)$$

where ϵ_v represents the permittivity of a vacuum. The first term of eq 4 represents work done for the point charge δq to be carried from $\mathbf{r}_0$ to $\mathbf{r}_1$ under $\mathbf{E}$, which is dependent on $\mathbf{r}_0$. In contrast, the second and third terms depend on only the structural parameter of the particle, $\mathbf{r}_1 - \mathbf{r}_2$. Because the third term of eq 4 does not contain $\mathbf{E}$ as a variable, the relationship of $\mu = \delta q(\mathbf{r}_1 - \mathbf{r}_0) + q(\mathbf{r}_1 - \mathbf{r}_2)$ is obtained. This relationship is essentially identical with the result obtained by the standard definition, eq 1, applying to the ionic species. The term $\delta q(\mathbf{r}_1 - \mathbf{r}_0)$ should not be included in μ because the magnitude of μ means a measure of how much electric energy is able to be stored in a mentioned particle and should depend only on its structural parameters. Then, setting the condition of $\mathbf{r}_1 = \mathbf{r}_0$ provides the relationship of $\mu = q(\mathbf{r}_1 - \mathbf{r}_2)$. However, most commercially available quantum chemical calculation programs take $\mathbf{r}_0$ to be the center of gravity ($\mathbf{r}_G$) for a calculated molecule or ionic particle as a matter of convenience.[9] The selection of $\mathbf{r}_G$ as $\mathbf{r}_0$ does not have essential physical meanings and possibly makes the unnecessary factor $q(\mathbf{r}_1 - \mathbf{r}_G)$ to be included in obtained values of dipole moments in calculations for ionic species. Because the employed calculation program will provide the values of $\mathbf{r}_1$ and $\mathbf{r}_G$, it is possible to obtain a corrected dipole moment, μ, by removing the factor $q(\mathbf{r}_1 - \mathbf{r}_G)$ from the value of dipole moment given by the program.

If one slightly modifies eq 1 as eq 1′, μ can be uniquely determined in also the case of ionic dipolar species.

$$\mu = \int_{\partial v}(\mathbf{r} - \mathbf{r}_{\delta q})\rho_{e(\mathbf{r})}\,d^3\mathbf{r} \quad (1')$$

$$\int_{\partial v}\rho_{e(\mathbf{r})}\,d^3\mathbf{r} = \delta q \quad (2')$$

where $\mathbf{r}_{\delta q}$ represents position vector for the center of electric charges possessing the positive or negative sign identical with that of δq of the mentioned ionic particle; in the case of the ionic species in Figure 1, $\mathbf{r}_{\delta q} = \mathbf{r}_1$. For electrically neutral molecules, $\delta q = 0$, the value of μ is of course independent of the selection of $\mathbf{r}_{\delta q}$.

The consideration above involves that ionic species also bear dipole moments if electric charges distribute asymmetrically as in the case of the ionic species in Figure 1. Then, it is possible that even completely dissociated small ionic species bear considerable dipole moments if the ionic species possess asymmetric electric charge distributions.

We have investigated aqueous solutions of a small organic salt, sodium *p*-toluenesulfonate (Na*p*TS), for dielectric relaxation behavior and have found profound dielectric relaxation behavior perfectly described by a Debye-type relaxation function in a frequency range much lower than the relaxation frequency of pure water molecules. Because the relaxation strength of the solution is proportional to the concentration (c) of Na*p*TS when c is lower than 0.4 M, the finding strongly suggests that dissociated pTS$^-$ keeps a significantly large dipole moment in aqueous solution. The finding should be new physicochemical significance and will be a key point for full understanding electric properties of aqueous electrolyte solutions containing small ionic species bearing dipole moments.

pTS$^-$ is a component of the monomer of a polyelectrolyte, sodium poly(styrenesulfonate) (NaPSS), and of a surfactant, sodium dodecylbenzene sulfonate (NaDBS), which are commonly used in industrial application and daily life. The finding is able to provide very important information to understand structure and dynamics in aqueous NaPSS solutions and also dynamics of micelle formation in aqueous NaDBS solutions. Furthermore, the presence of pTS$^-$ or salicylate ions (Sal$^-$) or both induces sphere to rodlike (or threadlike) shape transition of micelles in aqueous solutions of cationic surfactants, such as cetyltrimethylammonium bromide (CTAB).[10−13] To elucidate dielectric properties of pTS$^-$ will lead to full understanding of the mechanism of the sphere to threadlike shape transition of micelles in aqueous surfactant solutions.

Experimental Section

Materials. Na*p*TS was purchased from Wako Pure Chemicals Ltd. (Osaka) and was purified by recrystallization from a mixture of water and methanol. Highly deionized water with the specific resistance higher than 16 MΩ cm obtained by a Milli Q system (Nippon MilliPore, Tokyo) was used as a solvent of sample solutions for dielectric relaxation measurements. High-grade D_2O (99.9%) purchased from ISOTEC Inc. (Miamisburg, Ohio) was a solvent of a sample solution for spin−lattice relaxation time (T_1, ^{1}H NMR) measurements.

The concentration, c, of Na*p*TS for solutions for dielectric relaxation measurements ranged from 0.05 to 0.89 M and was 0.10 M for a D_2O solution for T_1 measurements.

Methods. Two measuring systems were employed for dielectric relaxation measurements. A system consisting of an RF LCR meter (4287A, Agilent Technologies) was operated in the frequency (ω) range from 6.28×10^6 to 1.00×10^{10} rad s^{-1}. In a higher ω range from 1.00×10^9 to 1.26×10^{11} rad s^{-1}, a dielectric material probe system (HP85070B consisting of a network analyzer, HP8720ES, Hewlett-Packard) was operated. In both systems, sample temperature was kept constant at 25 °C. Detailed measurement procedure was reported elsewhere.[14] The real and imaginary parts (ϵ' and ϵ'') of complex permittivity ($\epsilon^* = \epsilon' - i\epsilon''$) for sample solutions were estimated as functions of ω.

Dielectric spectra ($\Delta\epsilon'$ and $\Delta\epsilon''$) of pTS$^-$ in aqueous solution were evaluated in the form $\epsilon' = \Delta\epsilon' + f\epsilon_w'$ and $\epsilon'' = \Delta\epsilon'' + f\epsilon_w'' - \kappa_{DC}(\epsilon_v\omega)^{-1}$, where ϵ_w' and ϵ_w'' are the real and imaginary part of complex permittivity for pure water, respectively, and f represents fractional contribution of pure water to the dielectric relaxation. Moreover, κ_{DC} represents the direct current conductivity of the sample solution.

An NMR spectrometer, VARIAN UNITY600, was operated to measure T_1 of the ortho and meta proton of pTS$^-$ at 25 °C. The resonance frequency of the spectrometer was 600 MHz. A conventional inversion recovery pulse sequence was employed to determine T_1.

Densities of the aqueous Na*p*TS solutions (ρ) were measured as a function of c using a digital density meter (DMA5000, Anton Paar, Graz) at 25 °C to evaluate the partial molar volume of pTS$^-$.

To evaluate the optimized geometry for pTS$^-$, ab initio quantum chemical calculations were performed using Gaussian 98.[15] Geometry optimization was performed at HF/6-31G** level. Pictures of determined optimized geometries were generated by free software, Prax.[16]

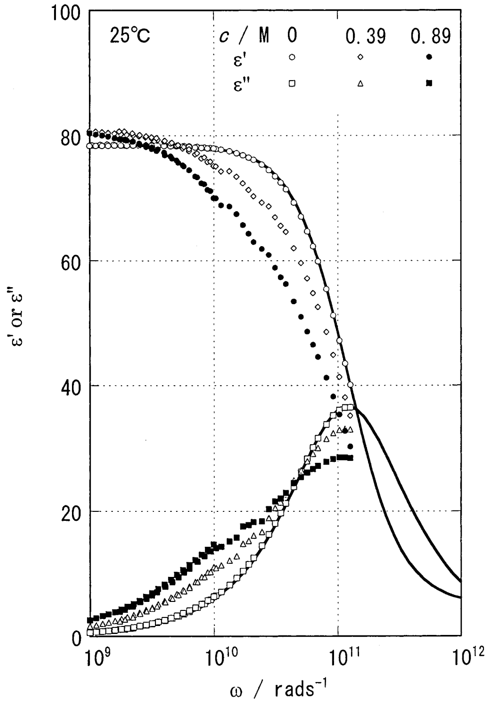

Figure 2. Dependencies of ϵ' and ϵ'' on ω for aqueous Na*p*TS solutions with $c = 0$, 0.39, and 0.89 M at 25 °C. Solid thick lines for a solution at $c = 0$ M (pure water) represent data found in the literature[17] at the same temperature.

Results and Discussion

Dielectric Relaxation Spectra. The dependencies of ϵ' and ϵ'' on ω for water ($c = 0$ M) and some aqueous Na*p*TS solutions ($c = 0.39$ and 0.89 M) are shown in Figure 2 as typical examples. Solid lines reproducing ϵ' and ϵ'' data for pure water represent the ω dependencies of published data[17] used as calibration curves for the measuring systems operated in this study. It is obvious that relaxation strength of free water molecules found around $\omega = 1.2 \times 10^{11}$ rad s^{-1} decreases dramatically with increasing c, whereas a new relaxation mode found around $\omega = 10^{10}$ rad s^{-1} increases its strength. As a result, the value of ϵ' in the low ω region does not change so much from that of pure water, $\epsilon_w' = 78$.

The dependencies of ϵ', ϵ'', $\Delta\epsilon'$, $\Delta\epsilon''$, $f\epsilon_w'$, and $f\epsilon_w''$ on ω for the solution at $c = 0.39$ M ($f = 0.885$) are shown as typical results in Figure 3. Two relaxation modes are observed in ϵ' and ϵ'' spectra at $\omega_f = 1.2 \times 10^{11}$ and $\omega_s = 1.15 \times 10^{10}$ rad s^{-1} as seen also in Figure 2. A fast mode of which the strength decreases with increasing c is assigned to the rotational relaxation mode of water molecules, $f\epsilon_w'$ and $f\epsilon_w''$. The relaxation time of the most preferential relaxation mode for pure water is $\tau_w = 8.3 \times 10^{-12}$ s (ω_f^{-1}) at 25 °C.[17] The other mode found at ω_s, of which relaxation time (τ_s) is essentially independent of c and relaxation strength ($\Delta\epsilon_s$) is proportional to c as shown later, is assigned to a relaxation mode caused by the presence of $p\mathrm{TS}^-$. The slow relaxation mode, $\Delta\epsilon'$ and $\Delta\epsilon''$, will be attributed to the rotational relaxation mode of $p\mathrm{TS}^-$ later. Here, we assume that the slow mode keeps the simplest single relaxation function described by Debye-type relaxation functions (eq 5) with a relaxation time $\tau_s = \omega_s^{-1} \approx 9.0 \times 10^{-11}$ s.

$$\Delta\epsilon' = \frac{\Delta\epsilon_s}{1 + \omega^2\tau_s^{\,2}} \qquad \Delta\epsilon'' = \frac{\Delta\epsilon_s\omega\tau_s}{1 + \omega^2\tau_s^{\,2}} \tag{5}$$

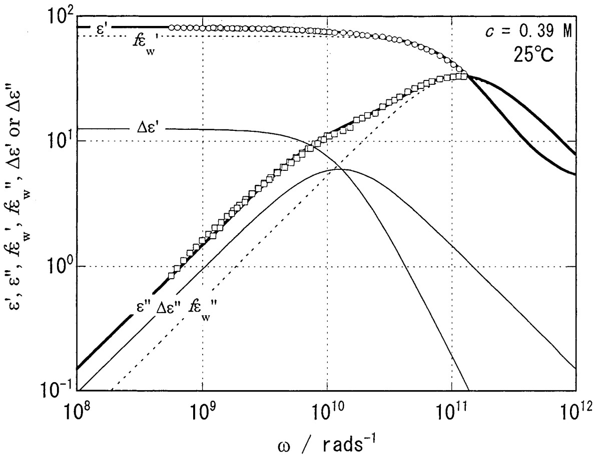

Figure 3. Dependencies of ϵ', ϵ'', $\Delta\epsilon'$, $\Delta\epsilon''$, $f\epsilon_w'$, and $f\epsilon_w''$ on ω for an aqueous Na*p*TS solution with $c = 0.39$ M at 25 °C. Broken lines for $f\epsilon_w'$ and $f\epsilon_w''$ are obtained by use of $f = 0.885$. Solid thin lines for $\Delta\epsilon'$ and $\Delta\epsilon''$ represent the best fit Debye-type relaxation functions (eq 5). Solid thick lines for ϵ' and ϵ'' are obtained by the sum of $\Delta\epsilon'$ and $f\epsilon_w'$ and $\Delta\epsilon''$ and $f\epsilon_w''$.

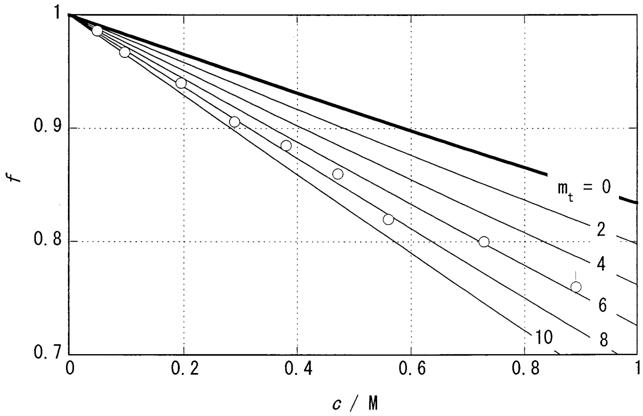

Figure 4. Relationship between f and c for aqueous Na*p*TS solutions at 25 °C. Each line for f is a predicted curve at variety of total numbers (m_t) of tightly hydrated water molecules to Na^+ and $p\mathrm{TS}^-$.

Solid thick lines perfectly reproducing experimental ϵ' and ϵ'' in Figure 3 are obtained by summing the contribution of the fast and slow relaxation modes, broken ($f\epsilon_w'$ and $f\epsilon_w''$) and solid thin ($\Delta\epsilon_s'$ and $\Delta\epsilon_s''$) lines. This involves the success of the assumption that the slow mode simply keeps the Debye-type relaxation. All of the spectra, ϵ' and ϵ'', obtained in this study are well decomposed into the two modes as observed in Figure 3. The dielectric spectra of water, $f\epsilon_w'$ and $f\epsilon_w''$, only in the solution at $c = 0.89$ M look slightly broader than those of the pure water; however, τ_w for the solution keeps the same value as that of the pure water.

In aqueous solution, Na*p*TS completely dissociates into Na^+ and $p\mathrm{TS}^-$ over a wide c range up to 0.98 M. Na^+ activity measurements for the aqueous solution using a sodium ion selective electrode easily confirmed the perfect dissociation of Na*p*TS in aqueous solution. Thus, the formation of ion pairs between Na^+ and $p\mathrm{TS}^-$ cannot be an essential reason for the relaxation behavior as considered in aqueous solutions of weak univalent electrolytes such as acetic acid.[18]

The dependence of f on c (Figure 4) is sensitive to the contribution of the volume fraction (v) of solutes and the total number of tightly hydrated water molecules (m_t) to the solutes. The contribution of v is well described by the relationship of $f = (1 - v)/(1 + 0.5v)$;[1] $v = \bar{v}_{\mathrm{Na}p\mathrm{TS}}c$, where $\bar{v}_{\mathrm{Na}p\mathrm{TS}}$ is the partial molar volume of the solute, Na*p*TS (ca. 116.67 cm^3 mol^{-1} at 25 °C). When solute particles bear m_t ($m_{\mathrm{Na}^+} + m_{p\mathrm{TS}^-}$) of tightly hydrated water molecules, which are dielectrically saturated or

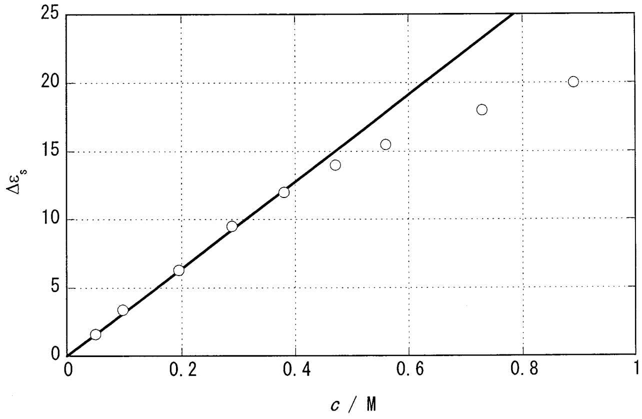

Figure 5. Dependence of $\Delta\epsilon_s$ on c for the aqueous NapTS solutions at 25 °C.

dead in the meaning of orientational polarizability, an additional factor of $-m_tc/55.6$ should be added to the value of f. Each line for f shown in Figure 4 represents the dependence of f on v and m_t. Agreement between experiments and the line obtained at $m_t = 8$ is reasonably good up to $c = 0.6$ M. The obvious deviation of f data from the line for $m_t = 8$ in a c region higher than 0.6 M is presumably related to the reduction of the number of tightly hydrated water molecules to pTS$^-$ or Na$^+$ or both.

Because the value of m_{Na^+} for Na$^+$ has been evaluated to be 4.5−6 at 25 °C, the value of $m_{p\mathrm{TS}^-}$ for pTS$^-$ should range from 2 to 3.5. Three decades ago, Pottel evaluated m_{Na^+} to be 5.7, 4.6, and 4.6 at 0, 25, and 50 °C, respectively, using the dielectric relaxation technique.[1] Very recently, Buchner et al.[19] have evaluated the value of m_{Na^+} to be 4.2 ± 0.3 in aqueous solutions of NaCl taking account of the kinetic depolarization effect. We also investigated the value of m_{Na^+} using the dielectric relaxation technique in aqueous NaBr solutions and obtained $m_{\mathrm{Na}^+} \approx 6$ at 25 °C neglecting the kinetic depolarization effect.[20] These suggest that the real value of m_{Na^+} ranges from 4.5 to 6. It is interesting to note that the average coordination number of water molecules around Na$^+$ in aqueous solution ($n_{\mathrm{Na}^+} \approx 6$) evaluated from scattering experiments[21] and computer simulations[22] is close to the value of m_{Na^+}, whereas in general the average coordination number of water molecules is not identical with the number of tightly hydrated water molecules to ions.

The relationship between $\Delta\epsilon$ and c for the aqueous NapTS solutions examined is shown in Figure 5. Up to $c = 0.4$ M, $\Delta\epsilon$ is perfectly proportional to c, while the $\Delta\epsilon$ data in a high c region deviate downwardly from the proportionality described with a solid line. This suggests that pTS$^-$ exists individually and rotates freely up to $c = 0.4$ M; however, possibly pTS$^-$ forms dimers, which have antiparallel dipole orientation and reduce the magnitude of dipole moments in a c region higher than 0.4 M. As described previously, Na$^+$ dissociates perfectly from pTS$^-$ until $c = 0.89$ M; therefore, the formation of ion pairs between Na$^+$ and pTS$^-$ is unlikely.

Figure 6 shows the dependence of τ on c for the aqueous NapTS solutions. The relaxation time, τ, is essentially independent of c even in the high c range in which $\Delta\epsilon$ is not proportional to c. There is possibility that the formation of larger molecular aggregates (trimer or tetramer) of pTS$^-$ bearing nonzero dipole moments in the high c range. However, if the larger aggregates of pTS$^-$ are formed, they exhibit dielectric relaxation processes with relaxation times longer than $\tau = 9.0 \times 10^{-11}$ s because of slow rotational modes caused by larger sizes of the aggregates. The fact that the value of τ is independent of c as seen in Figure 6 and no other relaxation modes possessing longer relaxation times are observed in the aqueous NapTS solutions does not support the formation of trimer or tetramer of pTS$^-$ in the high c region.

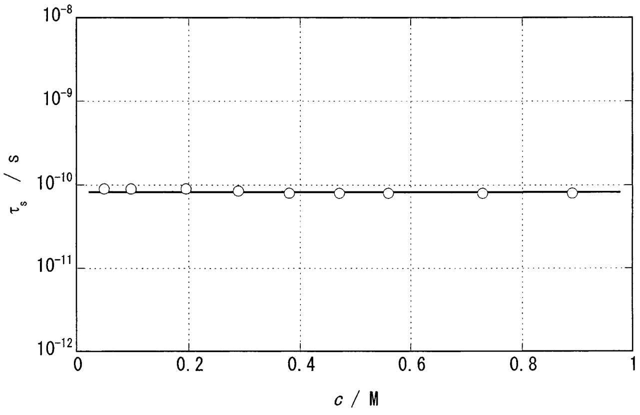

Figure 6. Dependence of τ_s on c for the aqueous NapTS solutions at 25 °C.

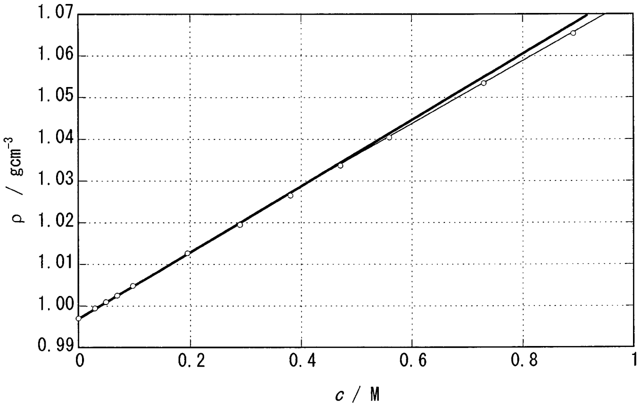

Figure 7. Relationship between the value of density, ρ, and c for the aqueous NapTS solutions at 25 °C.

When one very carefully looks at the relationship between the density of aqueous NapTS solutions, ρ, and c (Figure 7), a small break point is found out around $c = 0.5$ M. This break in the relationship between ρ and c might be relevant to changes of the solution structure in the high c region: (I) the formation of antiparallel dimer of pTS$^-$, (II) a change of the number of tightly hydrated water molecules to pTS$^-$, and (III) a change of the average orientation of the first neighbor water molecules surrounding pTS$^-$; this will be mentioned later. Although we have proposed the formation of antiparallel dimers of pTS$^-$ to explain the deviation from the proportionality in the relationship between $\Delta\epsilon$ and c seen in Figure 5, it seems that strong electrostatic repulsion between two pTS$^-$ ions overwhelms electric dipole−dipole interaction between them. Therefore, the possibility of the dimer formation might not be high in practice. Thus, changes of the solution structure such as suggestions II and III should be the essential reason for the deviation of $\Delta\epsilon$ data from the proportionality in the high c region seen in Figure 5.

Rotational Relaxation Time of pTS$^-$. Because the obtained ^{1}H NMR signals of pTS$^-$ are in a condition of extreme narrowing, eq 6 holds.[23]

$$\frac{1}{T_1} = \frac{(I+1)I\gamma_{\mathrm{H}}{}^4h^2\tau_c}{2\pi^2\lambda_{\mathrm{o-m}}{}^6} \qquad (6)$$

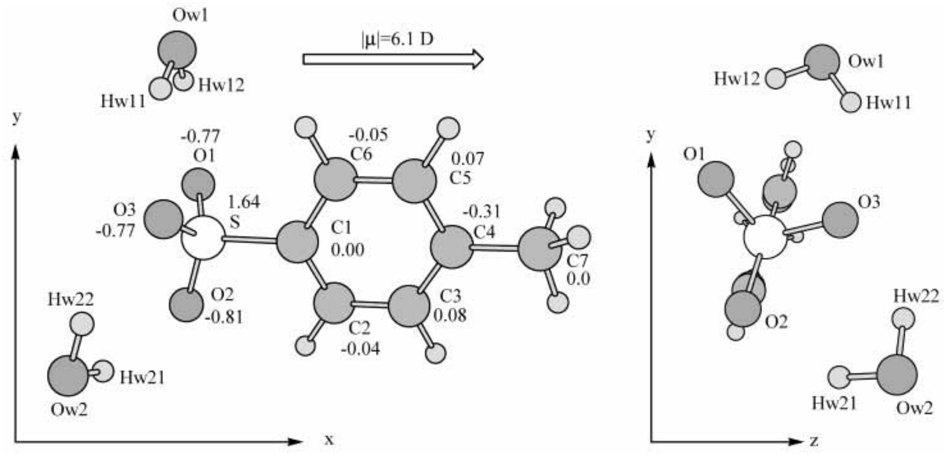

Figure 8. Optimized geometry of pTS$^-$ dihydrate obtained by ab initio calculations at HF/6-3G** level. The direction of arrows predicts that of the calculated dipole moment vector, μ. Numbers aside each heavy atoms represent the values of electric charges.

where I, γ_H, h, τ_c, and λ_{o-m} represent a spin quantum number ($^1/_2$ for ^{1}H), the gyromagnetic ratio of a proton, Planck's constant, the correlation time, and the distance between the ortho and meta protons, respectively. Consequently, the rotational relaxation time (τ_r) of pTS$^-$ in aqueous (D$_2$O) solution can be estimated from T_1 data using eq 6 and the relationship of $\tau_r = 3\tau_c$.

Because the two nuclei, ortho and meta proton, belonging to pTS$^-$ have magnetic dipole−dipole interaction with each other, the value of τ_r is directly related to (free) rotation of a molecular axis connecting the 1 and 4 carbon atoms. From the obtained value of T_1 (ca. 6.6 s), τ_r is evaluated to be 1.1×10^{-10} s, which reasonably agrees with the τ_s. Thus, we conclude that the mode of τ_s corresponds to the rotational relaxation mode of pTS$^-$. The reason that the value of τ_s obtained from the T_1 measurement is a little longer than that from the dielectric relaxation measurements is probably that the viscosity of D$_2$O is slightly higher than that of water at the same temperature.

Magnitude of Dipole Moment. Discussion on the relationship between the value of $\Delta\epsilon_s c^{-1}$ and magnitude of μ in the aqueous NapTS$^-$ solution is not easy at present because a general dielectric relaxation model that is valid in all of the solutions of polar solutes dissolved in polar solvents has not been established so far. However, the discussion on the values of $\Delta\epsilon_s c^{-1}$ and μ in particular systems on the basis of molecular models proposed[3,14,24−26] has been in progress.

We recently proposed a model that is essentially a combination of a Fröhlich's[27] and Kirkwood's models[28] and performs reasonably for the estimation of the magnitudes of μ for polar solutes such as trimethylamine oxide (TMAO)[29] and glycine betaine (GB)[26] in aqueous solutions. The final expression of the model given by eq 7 is identical with that of Oncley's model[24,25] that has been employed for the estimation of magnitude of dipole moments of biological molecules such as proteins in aqueous solution so far. According to the model, $\Delta\epsilon_s c^{-1}$ is given as the following equations.

$$\frac{\Delta\epsilon_s}{c} = \frac{AN_A\boldsymbol{\mu}^2}{2\epsilon_v kT} \tag{7}$$

$$A = 1 + \frac{|\boldsymbol{\mu}_w| z \cos\gamma}{|\boldsymbol{\mu}|} \tag{8}$$

where N_A and kT represent Avogadoro's number and a product between Boltzmann's constant and absolute temperature, respectively. Moreover, $|\boldsymbol{\mu}_w|$, z, and γ represent the magnitude of the dipole moment for a water molecule (ca. 1.84 D), the number of the first neighbor water molecules surrounding a tightly hydrated solute, and the average angle between the total dipole of a tightly hydrated solute and dipoles of the first neighbor water molecules. In the model, we suppose the first neighbor water molecules surrounding a (tightly hydrated) solute particle rotate at a relaxation rate not so much different from that of free water molecules in the bulk aqueous phase. The first neighbor water molecules have a certain finite cos γ value not zero, while free water molecules keep the cos γ value at zero.

The experimental value of $\Delta\epsilon_s c^{-1}$ is estimated to be $(32 \pm 1) \times 10^3$ cm^3 mol^{-1} from the slope of a straight line in Figure 5. The value of z can be roughly estimated from the average radius of an equivalent sphere for pTS$^-$ in aqueous solution ($r_{pTS^-} = 0.37$ nm) evaluated from the partial molar volume of pTS$^-$ ($\bar{v}_{pTS^-} = 122.96$ cm^3 mol^{-1}, cf. $\bar{v}_{Na^+} = -6.3$ cm^3 mol^{-1} at 25 °C[30]) in the manner $z = (4\pi/3)\{(r_{pTS^-} + 2r_w)^3 - r_{pTS^-}{}^3\}\rho_w \approx 35$,[26] where r_w and ρ_w represent the average radius of a water molecule (ca. 0.15 nm) and the number density of water molecules in the bulk state (ca. 3.35×10^{22} cm^{-3} at 25 °C). Because we do not have the precise value of cos γ for pTS$^-$ tightly hydrated by two or three water molecules in aqueous solution, we first assume the value of $\cos\gamma = 0.6$, which is adequate for both aqueous solutions of TMAO[29] and GB[26] possessing similar molecular sizes to that of pTS$^-$. Consequently, the magnitude of $|\boldsymbol{\mu}| = 7.6 \pm 0.2$ D is obtained for pTS$^-$ in aqueous solution and is larger by about 25% than 6.1 and 6.2 D, which are predicted for pTS$^-$ dihydrate or pTS$^-$ trihydrate by ab initio calculations described below. It is likely that this slight discrepancy results from a little underestimation of the cos γ or z values or both.

When one chooses the values of $\cos\gamma = 0.78$ and $z = 35$, $|\boldsymbol{\mu}| = 6.2 \pm 0.2$ D is evaluated for pTS$^-$ in aqueous solution through the value of $\Delta\epsilon_s c^{-1} = (32 \pm 1) \times 10^3$ cm^3 mol^{-1}. Moreover, in the simplest case of $\cos\gamma = 0$ (in other words, $A = 0$), $|\boldsymbol{\mu}| = 18.8 \pm 0.2$ D is obtained. Of course, the value of $\cos\gamma = 0$ is obviously underestimation for pTS$^-$ in aqueous solution because the size of pTS$^-$ is not as large as all the first neighbor water molecules orientated to pTS$^-$ at complete random. Kaatze et al.[3] employed an equation similar to eq 7, in which $A = {}^3/_2$, to evaluate the magnitude of μ for (ZnCl)$^+$ ions present in aqueous ZnCl$_2$ solutions. If we accept their equation with $A = {}^3/_2$, the value of $|\boldsymbol{\mu}| = 15.1 \pm 0.1$ is obtained. This value is twice as large as that predicted by the ab initio calculations. Consequently, it seems that the real value of cos γ is around 0.78.

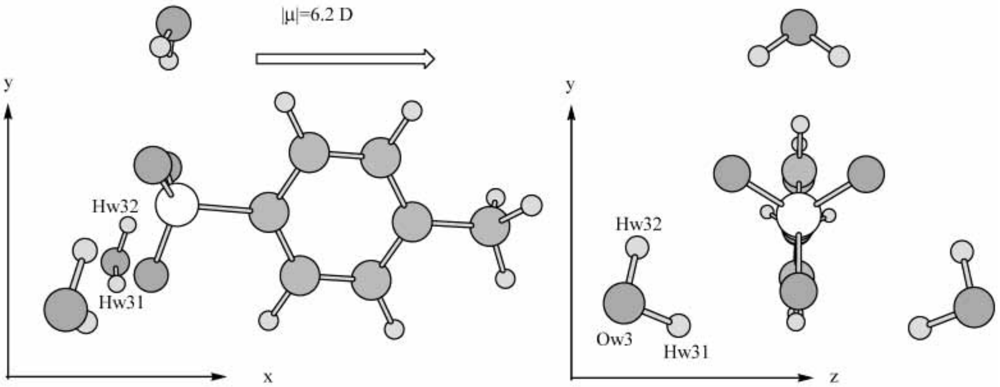

Figure 9. Optimized geometry of pTS$^-$ trihydrate obtained by ab initio calculations at HF/6-3G** level. The direction of arrows predicts that of the calculated μ.

TABLE 1: Some Important Parameters, Atomic Distances, Triangular and Dihedral Angles, and the Values of Components of Dipole Moments at the Optimized Geometries of pTS$^-$ Dihydrate (Figure 8) and pTS$^-$ Trihydrate (Figure 9)[a]

parameters	pTS$^-$ dihydrate	pTS$^-$ trihydrate
$\lambda_{\mathrm{S-C1}}$ (nm)	0.179	0.178
$\lambda_{\mathrm{C1-C2}}$ (nm)	0.138	0.138
$\lambda_{\mathrm{C2-C3}}$ (nm)	0.139	0.139
$\lambda_{\mathrm{C3-C4}}$ (nm)	0.138	0.139
$\lambda_{\mathrm{C4-C7}}$ (nm)	0.151	0.151
$\lambda_{\mathrm{Hw11-O3}}$ (nm)	0.220	0.221
$\lambda_{\mathrm{Hw12-O1}}$ (nm)	0.217	0.221
$\lambda_{\mathrm{Ow1-S}}$ (nm)	0.346	0.347
$\alpha_{\mathrm{Ow1-Hw11-O3}}$ (deg)	141.4	139.8
$\alpha_{\mathrm{Ow1-Hw12-O1}}$ (deg)	140.2	140.5
$\alpha_{\mathrm{Ow1-S-C1}}$ (deg)	96.0	95.6
$\beta_{\mathrm{Ow1-S-C1-C2}}$ (deg)	180.0	−178.7
$\lambda_{\mathrm{Hw21-O2}}$ (nm)	0.220	0.224
$\lambda_{\mathrm{Hw22-O3}}$ (nm)	0.221	0.222
$\lambda_{\mathrm{Ow2-S}}$ (nm)	0.356	0.357
$\alpha_{\mathrm{Ow2-Hw21-O2}}$ (deg)	142.3	141.5
$\alpha_{\mathrm{Ow2-Hw22-O3}}$ (deg)	142.2	142.1
$\alpha_{\mathrm{Ow2-S-C1}}$ (deg)	117.5	112.4
$\beta_{\mathrm{Ow2-S-C1-C2}}$ (deg)	59.9	61.6
$\lambda_{\mathrm{Hw31-O2}}$ (nm)		0.225
$\lambda_{\mathrm{Hw32-O1}}$ (nm)		0.221
$\lambda_{\mathrm{Ow3-S}}$ (nm)		0.357
$\alpha_{\mathrm{Ow3-Hw31-O2}}$ (deg)		141.1
$\alpha_{\mathrm{Ow3-Hw32-O1}}$ (deg)		142.6
$\alpha_{\mathrm{Ow3-S-C1}}$ (deg)		115.6
$\beta_{\mathrm{Ow3-S-C1-C2}}$ (deg)		−59.7
μ_x (D)	6.1 (10.7)[b]	6.2 (10.7)[b]
μ_y (D)	−0.2 (−0.6)[b]	−0.3 (−0.6)[b]
μ_z (D)	−0.3 (0.1)[b]	−0.1 (−0.1)[b]
$\lvert\boldsymbol{\mu}\rvert$ (D)	6.1 (10.7)[b]	6.2 (10.7)[b]
$\lvert -e_0(\mathbf{r}_- - \mathbf{r}_\mathrm{G})\rvert$ (D)	4.6	4.5

[a] Description for atoms and coordinates is presented in Figures 8 and 9. [b] Calculated values by Gaussian 98.

Quantum Chemical Calculations. Ab initio quantum chemical calculations are able to predict the optimized geometries of pTS$^-$ dihydrate and pTS$^-$ trihydrate as depicted in Figures 8 and 9. Some important atomic distances (λ_{i-ii}) and triangular ($\alpha_{i-ii-iii}$) and dihedral ($\beta_{i-ii-iii-iv}$) angles are summarized in Table 1; subscripts *i*, *ii*, *iii*, and *iv* represent related atoms as shown in Figures 8 and 9. Because hydrogen atoms of water molecules are fixed beside oxygen atoms of a sulfonate group, the origin for the hydration should be hydrogen bonding. The calculations also provide the vectors of dipole moment (μ) for individual pTS$^-$, pTS$^-$ dihydrate, and pTS$^-$ trihydrate at the optimized geometries as 7.3, 6.1, and 6.2 D in magnitude, respectively. Because the orientation of hydrated water molecules is almost perpendicular to the molecular axis of pTS$^-$, the presence of tightly hydrated water molecules does not influence the magnitude of μ so much in both pTS$^-$ dihydrate and pTS$^-$ trihydrate. As described in the Introduction, Gaussian 98 provides each component (μ_x, μ_y, and μ_z) of a dipole moment vector, $\boldsymbol{\mu}$, as a first derivative of the electrostatic energy with respect to an electric field applied to pTS$^-$ dihydrate and pTS$^-$ trihydrate in each direction, *x*, *y*, and *z*, values in parentheses in Table 1. Thus, μ can be determined, even if the mentioned molecule is not neutral but an ionic species. However, the values of $\boldsymbol{\mu}$ provided by Gaussian 98 contain an unnecessary term, $\delta q(\mathbf{r}_1 - \mathbf{r}_\mathrm{G})$, as described in the Introduction. The corrected values of each component of $\boldsymbol{\mu}$ by subtracting the value of $-e_0(\mathbf{r}_- - \mathbf{r}_\mathrm{G})$ are summarized in Table 1; e_0 and $\mathbf{r}_-$ represent the elementary charge and the position vector for the center of negative charges; the values of $\lvert -e_0(\mathbf{r}_- - \mathbf{r}_\mathrm{G})\rvert$ are also summarized in Table 1. The relatively large magnitudes of the corrected $\boldsymbol{\mu}$ are crucial evidence for the finding that pTS$^-$ exhibits pronounced dielectric relaxation.

The heat of hydrogen bond formation (ΔH) between a water molecule and sulfonate ion can be evaluated by using a conventional counterpoise method,[31] which can adequately correct basis set superposition error. The obtained values of ΔH are −6.63 and −6.46 kcal mol^{-1} on the average for each OH···OS-type hydrogen bonding in pTS$^-$ dihydrate (Figure 8) and pTS$^-$ trihydrate (Figure 9), respectively. In the procedure of ΔH value calculations, the contribution of the slight rotation of a sulfonate group around the C1−S bond is not taken into account. If one takes account of the contribution of the rotation of a sulfonate group to the formation energy, the values of 6.33 and 6.26 kcal mol^{-1} are obtained for pTS$^-$ dihydrate and pTS$^-$ trihydrate, respectively. Although the absolute values of these ΔH are not as high as those for usual hydrogen bonding, each water molecule forms two hydrogen bonds between a sulfonate ion and is fixed tightly in both pTS$^-$ dihydrate and pTS$^-$ trihydrate. From these, we conclude here that pTS$^-$ exists in aqueous solution in the form that is tightly hydrated by two or three water molecules and has similar shapes to the optimized geometries of pTS$^-$ dihydrate (Figure 8) or pTS$^-$ trihydrate (Figure 9).

Numbers shown beside each heavy atom in Figure 8 represent the determined electric charges for each heavy atom of pTS$^-$, assuming electric charges of hydrogen atoms included in heavy atoms. The sum of electric charges belonging to a toluene part is −0.29, while that belonging to a sulfonate ion part is −0.71. Because the toluene part is much more positively charged relative to the sulfonate ion part, the fact the calculated direction of dipole moment is arranged toward the toluene part is comprehensive.

Last of all, because we have found that a salicylate ion, Sal$^-$, also keeps a relatively large dipole moment and shows profound dielectric relaxation behavior in aqueous solution, as well as pTS$^-$, we believe many other small ions keep respectable dipole moments in aqueous solution.

Concluding Remarks

Dissociated pTS$^-$ in aqueous solution shows pronounced dielectric relaxation behavior well-described with a Debye-type relaxation function. The value of the dielectric relaxation time for pTS$^-$ is very close to the rotational relaxation time determined from a spin−lattice relaxation time, T_1. The number of tightly hydrated water molecules to pTS$^-$ in aqueous solution is evaluated to be 2−3.5 from the concentration dependence of dielectric relaxation strength. Thus, pTS$^-$ is tightly hydrated by water molecules and keeps large dipole moment in aqueous solution. Ab initio quantum chemical calculations provide the optimized geometries of individual pTS$^-$, pTS$^-$ dihydrate, and pTS$^-$ trihydrate and calculate the magnitudes of μ to be 7.3, 6.1, and 6.2 D, respectively. These large calculated values are crucial evidence for the fact that pTS$^-$ keeps large μ in aqueous solution.

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