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Measurement of the Dielectric Relaxation Property of Water−Ion Loose Complex in Aqueous Solutions of Salt at Low Concentrations

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Electrolytes and their dissociated ions are thought to form positive or negative hydration layers around them. In this study, we have developed a method to determine the volume and the dielectric relaxation property (relaxation frequency f_c, dispersion intensity δ) of the water hydrating ions in salt solutions. The method consists of four steps:
(1) By use of a high-resolution microwave dielectric spectroscopy technique, the dielectric spectra of sample salt solution and bulk water are measured in pair.
(2) The dielectric spectrum of solutes (ions) with water layers for a given volume fraction ϕ is then calculated from each pair of dielectric spectra of a sample salt solution and reference water according to the Hanai mixture theory.
(3) Each spectrum of solutes with water layers at a given ϕ is decomposed into a few Debye relaxation functions and the bulk water component.
(4) The volume fraction ϕ is operationally decreased from 0.5, and steps (2) and (3) are repeated at each ϕ until the bulk water component vanished. Then the volume fraction of the hydrated solutes (ions) in solution is determined.
The method was applied to NaF and NaCl solutions. As a result the different spectral intensity was nearly proportional to the salt concentration below 0.2 M in the frequency range of 3−26 GHz. The hydration number N_h and the dielectric relaxation property of the hydration layer for each salt solution was successfully determined as $(f_{c1}, \delta_1, N_h) = (18.7, 44.9, 27.9)$ for NaCl and $(f_{c1}, \delta_1, f_{c2}, \delta_2, N_h) = (26.0, 6.70, 5.64, 19.2)$ for NaF.

Introduction

Interactions between an ion and surrounding water molecules have been discussed over a century.[1,2] The negative hydration concept by Samoirov[3] and a hydration model of water−structure breaking ions by Frank and Wen[4] were proposed to discuss the hydration states of large halogen or alkali ions, so-called chaotropic ions. Both ideas give us a similar image of loosening hydrogen bond networks connecting water molecules around ions. Those aqueous solutions were found to have higher dielectric relaxation frequencies than bulk water by microwave spectroscopy.[5−8] Wei et al. measured the dielectric spectra of alkali chloride (A = Li, Rb, and Cs) aqueous solutions above 0.33 M up to 5 M and found nonlinear concentration dependence of dielectric constatnt and continuous decrease of τ_D with increasing salt (ACl) concentration for Rb and Cs.[9] Buchner and Barthel assigned the absorption peaks of salt solutions for ion-pair formation in the sub-gigahertz range and cooperative orientation of water molecules at 10−20 GHz.[8,10,11] Wachter et al. examined chaotropic salt solutions by microwave dielectric spectroscopy in the concentration range from 0.05 to 1.5 M but did not detect clear anionic effects.[12]

Salt solutions of relatively high concentrations have so far been studied with microwave dielectric spectroscopy because of the limited resolution of instruments. However, at high salt concentrations there may be no bulk water free from the effects of ions in solution. Thus, the volume of the water influenced by ions with different dielectric relaxation properties from that of bulk water is basic quantitative information as an extended concept of hydration shells for understanding many salt effects in solution chemistry.

Recently we have developed a technique of high-resolution microwave dielectric spectroscopy. In this study we applied this technique to measure the dielectric spectra of the aqueous solutions of salts in the low salt concentration range. In this range the difference between the complex dielectric spectrum of the salt solution and that of purified water (by milli Q, Millipore) should be proportional to the salt concentration in the frequency range above ∼3 GHz where the dielectric contributions of ionic conduction and Hubbard Onsager effects that follow the limiting law are much smaller compared to those of the orientational relaxation of water molecules.[9] We first examined the proportionality between the salt concentration and the difference dielectric spectrum of salt solution against the water spectrum. We then tried to evaluate the volume and the dielectric relaxation property of hydration water around ions.

Experimental Section

Aqueous Solutions of Salts. NaF (purity 99.0%) and NaCl (99.5%) were purchased from Wako Chemical and dried in a vacuum chamber of ∼1 mPa at room temperature for 24 h and

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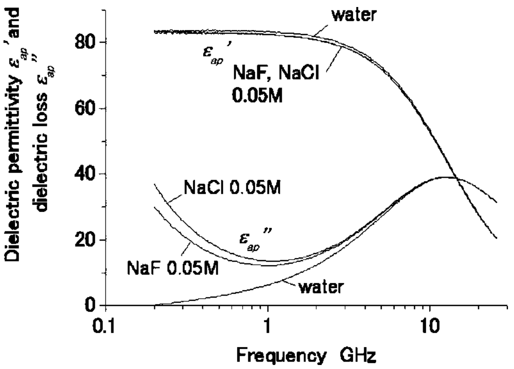

Figure 1. Dielectric spectra $\varepsilon_{ap}*(f)$ of NaCl and NaF aqueous solutions.

dissolved in purified water by milliQ (Millipore) at concentrations from 0.05 to 0.2 mol/L. Each solution was degassed and introduced in the measurement glass cell. The partial specific volume (s_v) of each salt in water was calculated from the solution density measured with an Anton-Paar DMA-58 density meter.

Dielectric Spectroscopy. All measurements were made in a conically shaped glass cell (total volume, 3.2 mL) at 10.0 ± 0.01 °C (Neslab, RTE-17, thermocontrolled circulator) and connected to a microwave network analyzer (Agilent, PNA8364B-85070E). The temperature was chosen to detect a hypermobile component having a higher relaxation frequency than 12.6 GHz of bulk water. An open-end coaxial flat surface probe (Agilent, high-temperature type, 19 mm in diameter, electric length ~45 mm) was mainly used for the measurements in the frequency range 0.2−26 GHz (301 frequency points) after three calibration steps of open, short, and pure water at 10.0 ± 0.01 °C. Those spectra were recorded as previously described.[13,14] In short, the spectra of the reference water ($\varepsilon^*_w(f)$) and salt solution ($\varepsilon^*_{ap}(f)$) were measured in pairs 8−16 times to reduce machine drift noise over 3−6 h at a given concentration of a given salt solution as shown in Figure 1. The differences were very small but systematic (Figure 2). The difference spectrum for each pair was calculated by

$$\Delta\varepsilon^*(f) = \Delta\varepsilon'(f) - i\Delta\varepsilon''(f) = \varepsilon^*_{ap}(f) - \varepsilon^*_w(f) - i\frac{\sigma}{2\pi f\varepsilon_0} \quad (1)$$

where σ is basically the static electrical conductivity of a given salt at a given concentration. In this study the value σ was adjusted to make $\Delta\varepsilon''$(0. 2GHz) = 1. By this treatment small dielectric absorption peaks in the sub-gigahertz range became obvious, if any, although a $1/f$ function was added on the absolute peak heights. It causes only a small effect on the absorption peak heights in the higher frequency range from 3 to 26 GHz. The difference spectra by eq 1 were then averaged and smoothed to eliminate the resonance noise from 2 to 6 GHz arisen from the probe by referring two spectral curves of the same salt solution taken by two probes with 45 and 210 mm electric lengths. Then the smoothed spectral curves were determined using fifth−eighth order polynominal functions of log(f) as shown in Figure 2A. Figure 2B shows the error curves $s_e*(f) = (s_e'(f), s_e''(f))$ corresponding to the spectral curves of $\Delta\varepsilon'$ and $\Delta\varepsilon''$. The difference dielectric spectra of NaCl and NaF solutions at different concentrations are presented in parts A and B of Figure 3. Parts A and B of Figure 4 show the concentration dependences of $\Delta\varepsilon'$ and $\Delta\varepsilon''$ at 10 sampled frequencies. Both the $\Delta\varepsilon'$ and $\Delta\varepsilon''$ for NaCl and NaF were found to have dominant linear relation to the salt concentration below 0.2 M, suggesting that particlelike solutes are dispersed in water as shown by the Hanai mixture theory.[15] Thus, we adopt the Hanai mixture theory to analyze the average dielectric relaxation property of hydrated ions in bulk water.

Method of Analysis. We analyze the results with the following assumptions: (1) Salts (sodium halides) are completely dissociated in water in the concentration range <0.2 M. (2) Anions and cations are homogeneously dispersed in water. (3) Each ion interacts weakly or strongly with a finite number of the surrounding water molecules to form a loosely assembled water−ion complex, hereafter called water−ion loose complex, having different dielectric property from that of bulk water. The volume fraction of such water−ion loose complex in a salt solution should then be proportional to the salt concentration. Here we adopt the Hanai mixture theory extended in ϕ range from Wagner theory[16] ($0 < \phi \ll 1$) for the systems of volume fractions ($0 < \phi < 1$) of spherical particles. In our case the spherical particles can simulate hydrated ions in water. The apparent complex dielectric permittivity of the water−ion loose complex is given by eq 2.[15] Of course in the solution there are hydrated anions and hydrated cations. The fraction of contact ion pair would be negligibly small in the concentration range below 0.2 M.[11,17] The complex dielectric permittivity of a multicomponent solution can be simulated by mixing the first solute particles of volume fraction ϕ_1 in water and then mixing the second solute particles of ϕ_2 in the solution and so on. The total volume fraction ϕ of the hydrated solutes is given by $\phi = \sum_{i=1}^{n} \phi_i$, where n is the number of solute species, along with the Hanai theory. In this study we estimate ε^*_q as the complex dielectric permittivity of hydrated solutes by convoluting hydrated anions and hydrated cations. This method is effective in evaluating the volume fraction of total hydrated solutes without assuming dielectric properties other than Debye relaxation processes.

ϕ Scanning Analysis. The dielectric spectrum $\varepsilon^*_{ap}(f)$ of a salt aqueous solution was mathematically split into a bulk water spectrum $\varepsilon^*_w(f)$ and that of solute with a water layer $\varepsilon^*_q(f)$ at arbitrary volume fraction ϕ by eq 1 of the Hanai mixture theory.[14,15] When ϕ is much larger than the real volume fraction ϕ_B of hydrated solute ions in solution $\varepsilon^*_q(f)$ is close to $\varepsilon^*_w(f)$, which has an absorption peak at $f = f_{c_0}$ = 12.6 GHz. If we operationally decrease ϕ from a large value ($\phi \gg \phi_B$), $\varepsilon^*_q(f)$ should approach and become very close to the real spectrum of the hydrated solute at $\phi = \phi_B$, where the bulk component should vanish. This operational procedure is referred to as ϕ scanning analysis, and its details including the determination of ϕ_B are explained in the next section. Thus, one may see the dielectric absorption peak shifting to higher or lower frequency than f_{c_0} depending on the solute character.

$$\varepsilon^*_q = \left\{\varepsilon^*_{ap} - (1-\varphi)\left(\frac{\varepsilon^*_{ap}}{\varepsilon^*_w}\right)^{\frac{1}{3}}\varepsilon^*_w\right\} \Big/ \left\{1 - (1-\varphi)\left(\frac{\varepsilon^*_{ap}}{\varepsilon^*_w}\right)^{\frac{1}{3}}\right\} \quad (0 \ll 1) \quad (2)$$

The number of water molecules in the region which dielectric property was affected by a pair of Na$^+$ and X$^-$ can be calculated by eq 3

$$N_h = \frac{55.6(\varphi_B - v)}{c} \quad v = \frac{cM_w s_v}{1000} \quad (3)$$

where 55.6, c, v, s_v, and M_w are the molar concentration of bulk water in mol/L, the salt concentration in mol/L, the partial

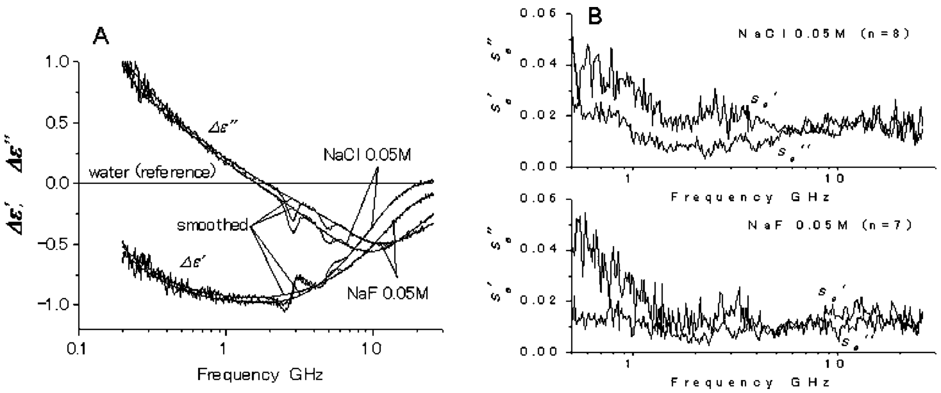

Figure 2. Difference spectra of NaCl and NaF solutions. (A) Difference dielectric spectra ($\Delta\varepsilon' = \varepsilon_{ap}' - \varepsilon_w'$, $\Delta\varepsilon'' = \varepsilon_{ap}'' - \varepsilon_w''$) averaged over n experiments and their smoothed curves. (B) Standard errors of the difference spectra of NaCl 0.05 M ($n = 8$) and NaF 0.05 M ($n = 7$) corresponding to A.

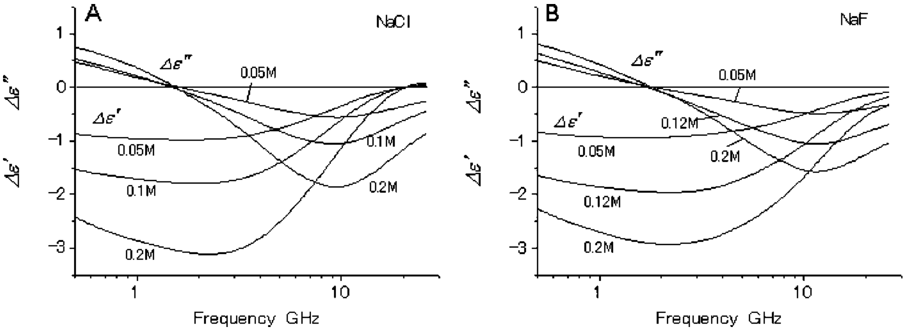

Figure 3. Difference dielectric spectra of salt solutions. (A) NaCl solutions. (B) NaF solutions.

volume fraction of dissociated salt in water measured from the solution density, the partial specific volume of dissociated salt in water in mL/g, and mass weight of salt, respectively. The solute shape causes a small influence on the N_h value. There is only a few percentage difference in the N_h values between spherical shape and ellipsoidal shape of axial ratio of 3:1 for same ϕ as discussed in the previous paper.[18]

Debye Component Analysis. At certain ϕ, $\varepsilon_q^*(f)$ was decomposed into a series of Debye functions and the bulk water component (DW spectrum, $f_{c0} \approx 12.6$ GHz, $\delta_0 \approx 77.5$, at 10 °C) in the range from 3 to 26 GHz

$$\varepsilon_q^*(f) \cong \varepsilon_{q_{sim}}^*(f) = \varepsilon_{q_{inf}} + \alpha(\varepsilon_w^*(f) - \varepsilon_{w_{inf}}) + \sum_{j=1}^{m} \frac{\delta_j}{1 + i(f/f_{cj})} - i\frac{\sigma_1}{2\pi f \varepsilon_0} \quad (4)$$

where $\varepsilon_{winf} = 5.5$ at 10 °C according to the literature.[19] σ_1 is an adjusting parameter as the interfacial excess conductivity. εqinf was set equal to 5.5 because the Wagner eq 5 gives values only a little different from ε_{winf} based on a shelled-sphere model[19−21]

$$\varepsilon_{q_{inf}} \approx \varepsilon_{w_{inf}} \frac{2(1 - \upsilon/\varphi)\varepsilon_{w_{inf}} + (1 + 2\upsilon/\varphi)\varepsilon_i}{(2 + \upsilon/\varphi)\varepsilon_{w_{inf}} + (1 - \upsilon/\varphi)\varepsilon_i} \quad (5)$$

Here ε_i is the average dielectric constant of salt ions in water at high frequency limit, ε_i was approximately estimated from the refractive indices of salt crystals taking into account the atomic packing such as 2.5 for NaF, 3.2 for NaCl. If $\upsilon/\phi_B \ll 1$, $\varepsilon_{q_{inf}}$ is insensitive to ε_i, then $\varepsilon_{qinf} \approx \varepsilon_{winf}$.

At arbitrary ϕ, best fit combinations of (f_{c_i}, δ_i) and α were searched on the dispersion curves $\varepsilon q'(f)$ using an evaluation function $E_{rr} = \sum_{n=1(f=3\text{GHz})}^{n=159(f=26\text{GHz})} w(f)(\varepsilon' q'(f) - \varepsilon q'_{sim}{}'(f))^2$. Here a weighting function $w(f) = f$ was used. Judgment whether the fitting was successful was made by examining $E_{rr} < 100c/\phi$. Initially the number m of Debye functions in eq 4 was one.

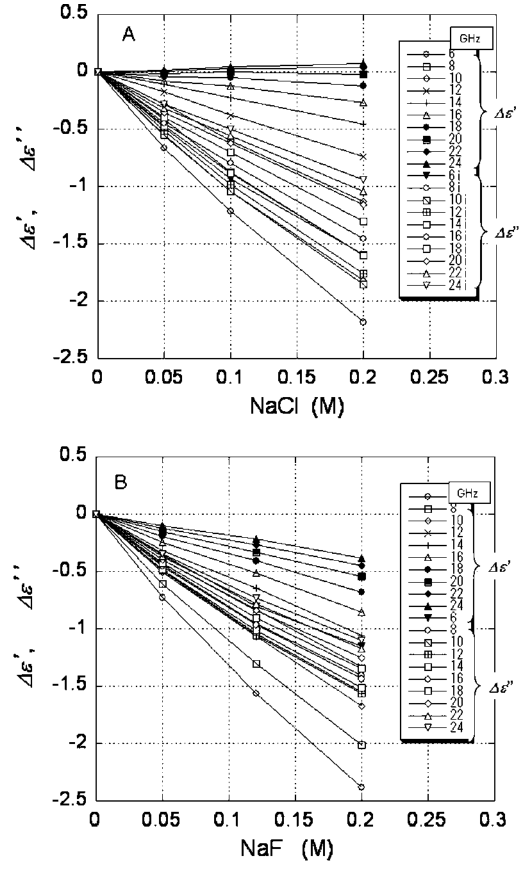

Figure 4. Concentration dependence of Δε' and Δε'' of salt soluitons. (A) NaCl. (B) NaF.

TABLE 1: Dielectric Relaxation Parameters of Hydrated Solutes (Water−Ions Complex) in NaCl and NaF Solutions

	f_{c_2} (GHz)	δ_2	f_{c_1} (GHz)	δ_1	ϕ_B/c (M^{-1})	N_h
$NaF_c = 0.05$ M	6.70	5.64	19.9	26.0	0.332 ± 0.015	19.2 ± 0.9
$NaCl_c = 0.05$ M			18.7	44.9	0.510 ± 0.026	27.9 ± 1.5

TABLE 2: Molar Volume Fraction of Hydrated Solutes in Solutions[a]

	ϕ_B/c (M^{-1})	N_h
NaCl, 0.05 M	0.510	27.9
NaCl, 0.20 M	0.425	22.7
NaF, 0.05 M	0.332	19.2
NaF, 0.20 M	0.294	16.6

[a] The values were estimated above 6 GHz based on the parameters in Table 1. N_h is the number of hydrating water molecules per ion pair.

When the deviation was larger than the allowable error E_{rr} in the best-fit condition, m was increased by one. This process was repeated until the fitting curve agreed with the experimental curve within the allowable error E_{rr}. We adopted $m = 1$ for NaCl and $m = 2$ for NaF in this study. As noted previously with decreasing ϕ from a sufficiently large value $\phi \gg \phi_B$ toward v with a small step the bulk component factor α must decrease and should change its sign from plus to minus at $\phi = \phi_B$. Thus, the outer boundary of the water region dielectrically affected by ions was determined for each solution.

To examine the accuracy of this method we made the following calculations. First, a spherical particle of radius a has the following dielectric relaxation property

$$\varepsilon_s^*(f) = 5.5 + \frac{\delta_1}{1 + i(f/f_{c_1})} + \frac{\delta_2}{1 + i(f/f_{c_2})} \tag{6}$$

Second, this sphere is covered with a water layer of thickness $(b-a)$ that has the dielectric property

$$\varepsilon_w^*(f) = 5.5 + \frac{\delta_0}{1 + i(f/f_{c_0})} \tag{7}$$

The whole complex dielectric permittivity $\varepsilon^*_{q_{sim}}$ of the shelled sphere of radius b is given by the following equation by electrostatics

$$\varepsilon^*_{q_{sim}} = \varepsilon^*_w \frac{2(1-(a/b)^3)\varepsilon^*_w + (1+2(a/b)^3)\varepsilon^*_s}{(2+(a/b)^3)\varepsilon^*_w + (1-(a/b)^3)\varepsilon^*_s} \tag{8}$$

Then $\varepsilon^*_{q_{sim}}$ was decomposed into two Debye components (f'_{c1}, δ'_1, f'_{c2}, δ'_2) and a water component by the present method using eq 4. For example putting (f_{c1}, δ_1, f_{c2}, δ_2)= (19.9, 26.0, 6.70, 5.64) according to Table 1, when $(a/b)^3$ was increased from 0.80 to 1, estimated values of f'_{c1} and f'_{c2} varied linearly from 21.75 and 5.82 to 19.9 and 6.70, respectively. Thus, the present linear decomposition method can estimate accurate values of relaxation frequencies f_{c_1} and f_{c_2} of the hydrated solute.

Results and Discussion

Proportionality between $\Delta\varepsilon^*(f)$ and c. The difference spectra for each salt were shown in Figure 2A. Figure 2B shows that the standard errors $s_e'(f)$ and $s_e''(f)$ of $\Delta\varepsilon'$ and $\Delta\varepsilon''$ were less than 0.03 and 0.02, respectively, in the range from 2 to 26 GHz. $\Delta\varepsilon'$ and $\Delta\varepsilon''$ for each salt were replotted for ten sampled frequencies as a function of salt concentration c. Figure 3 shows the difference spectra at different salt concentrations. In Figure 4 the proportionality between $\Delta\varepsilon^*$ and c was confirmed for NaCl $c \leq 0.1$ M within the error in the frequency range from 3 to 26 GHz and for NaF $c \leq 0.05$ M. Above $c = 0.1$ M $\Delta\varepsilon'$ and $\Delta\varepsilon''$ were found to deviate slightly from the linear relations. As for NaCl solutions the difference spectrum of 0.05 M multiplied by 1.85 and that of 0.2 M multiplied by 0.565 well agreed with that of 0.1 M, while for NaF solutions that of 0.05 M multiplied by 2.20 and that of 0.2 M multiplied by 0.66 well agreed with that of 0.12 M in the range from 3 to 26 GHz. Therefore Debye component analyses were made for 0.05 M solutions and summarized in Tables 1 and 2. These results indicate that the volume of the water dielectrically influenced by a solute particle (an anion or a cation or both ions in pair) is finite and can be determined in the salt concentrations $c \leq 0.2$M.

ϕ Scanning Analysis. According to eq 2, with decreasing ϕ from 0.10 to 0.02 with a small step ($\Delta\phi = -0.01$) the dielectric spectra of solute (ions) with a water layer were calculated as shown in parts A and B of Figure 5. For both cases the absorption peaks shifted to the higher frequency than that of bulk water ($f_{c_0} \approx 12.6$ GHz) with decreasing ϕ. When ϕ is smaller than ϕ_B (e.g., $\phi/c \leq 0.4$ for NaCl 0.05 M) the dispersion curves cannot be simulated with eq 4 using positive parameters. By lowering the volume fraction ϕ, the fraction of bulk component α decreased and became zero while f_{c_1} and f_{c_2} changed slightly as shown in Figures 6 and 7. The volume fraction of hydration boundary ϕ_B for each solution was determined from the x-axis intercept of α for example $\phi_B/c = 0.510 \pm 0.026$ for 0.05 M NaCl solution as seen in Figure 6B and $\phi_B = 0.332 \pm 0.015$ for 0.05 M NaF solution as seen in Figure 7B and summarized in Table 1. Parts A nd B of Figure 8 show the resulting spectra $\varepsilon_q^*(f)$ of the hydrated solutes which have different dielectric properties from that of bulk water in NaCl and NaF solutions. The spectra $\varepsilon_q^*(f)$ for NaCl was simulated by one Debye components (f_{c_1}), while the spectra of NaF required two Debye components. Although Na^+ and F^- ions are commonly classified into water-structure makers, surprisingly a hypermobile component ($f_{c_1} > f_{c_0}$) was dominant for both NaF and NaCl solutions, and only one Debye function (f_{c_1}) could simulate the spectra above 3 GHz for NaCl. It was unexpected that different relaxation components corresponding to the hydration shells of Na^+ and Cl^- were not observed. This suggests that 19−28 water molecules on average dynamically interact with a pair of anion and cation and together form a water/ion-pair loose complex that differs in relaxation property from the bulk water at salt concentrations below 0.1 M. This interpretation is not necessarily inconsistent with earlier studies which used, for example, compressibility[22] or NMR[23] measurements, which could only detect tightly bound water, and the results thus obtained were analyzed by assuming simple models to estimate the hydration numbers of anion and cation separately. In our analysis of the present data, however, the results suggest the existence of waters with dielectric relaxation frequency (f_{c_1}) higher than that of bulk water as well as tightly bound waters with f_{c_2} or lower. Taken together, we cannot exclude a possibility that in aqueous solution hydrated cation and anion behave as not totally independent entities but rather more or less interact

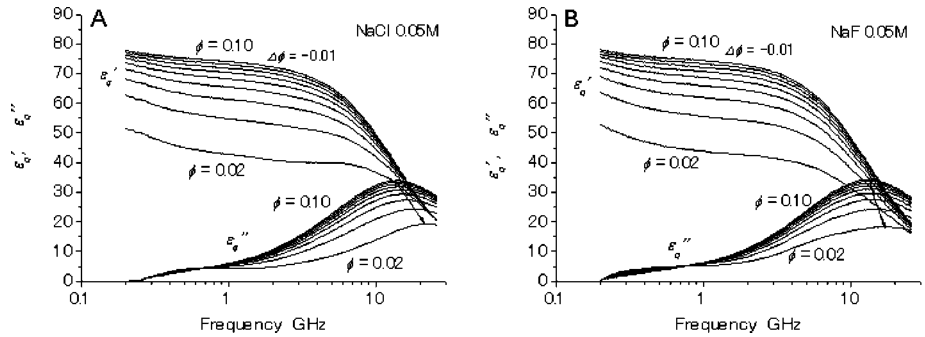

Figure 5. ϕ scanning spectral curves of NaCl and NaF solutions.The arrows indicate high-frequency shifts of absorption peaks with decreasing ϕ.

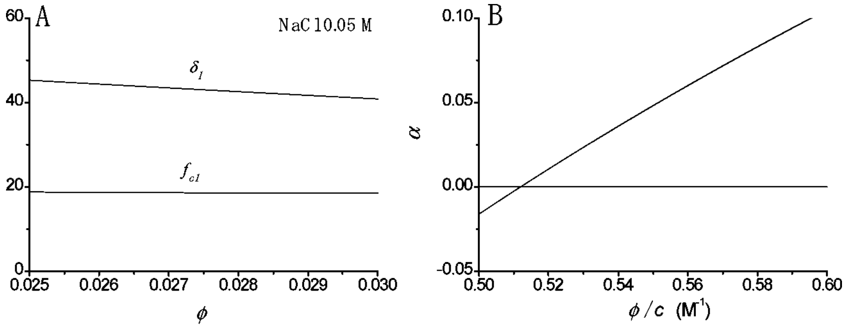

Figure 6. Best-fit parameters vs ϕ and determination of the hydration boundary in NaCl 0.05 M solution. (A) Parameters of two debye components. (B) Volume fraction where bulk water component $\alpha = 0$ was determined as $\phi/c = \phi_B/c = 0.510$ by the linear fitting line.

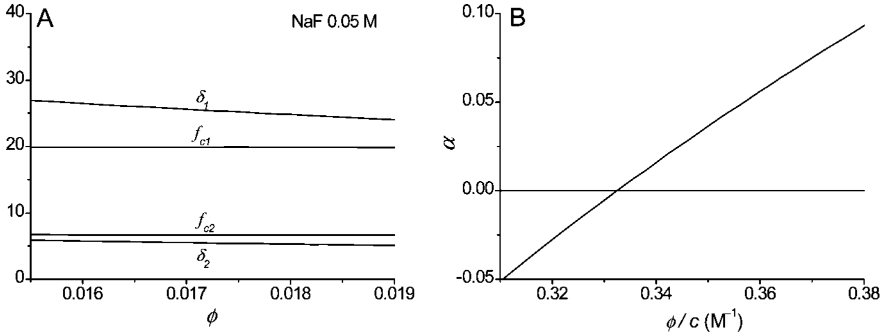

Figure 7. Best-fit parameters vs ϕ and determination of the hydration boundary in NaF 0.05 M solution. (A) parameters of three debye components. (B) Volume fraction where bulk water component $\alpha = 0$ was determined as $\phi/c = \phi_B/c = 0.332$ by the smoothed line.

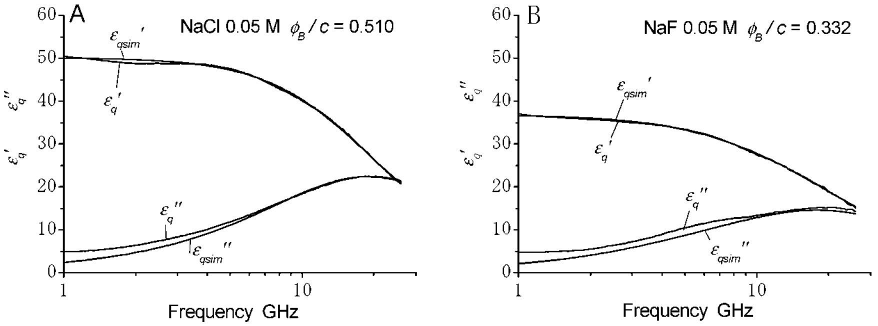

Figure 8. Dielectric spectra of a water−ion complex in NaCl and NaF solutions. (A) NaCl 0.05 M, $\phi_B/c = 0.510$. (B) NaF 0.05 M, $\phi_B/c = 0.332$. Simulation spectrum by eq 3: $\varepsilon_{q_{sim}}* = \varepsilon_{q_{sim}}' - I\varepsilon_{q_{sim}}''$.

with each other, and hence it seems hardly appropriate to divide the observed number N_h between cation and anion.

In the range from 0.2 to 1 GHz one Debye component was detected for each solution such as (f_{c_3}, δ_3) = (0.45, 7.5) for NaF and (0.40, 7.4) for NaCl. Here the parameters of subgigahertz components (f_{c_3}, δ_3) are not accurate because of the adjusting $1/f$ function in eq 4. These f_{c_3} components are probably due to the relaxation of ionic atmosphere as previously reported.[11,17]

Conclusion

In this study a method to determine the volume fraction and the dielectric relaxation property of the hydration water in an aqueous solution of salt at low concentration has been developed by combining an emulsion theory and Debye component analysis for the dielectric spectra measured by a high-resolution spectrometer. ϕ scanning analysis tells us an overall feature of the dielectric relaxation property of solutes in solvent. The present method was applied to analyze the dielectric spectra of 0.05−0.2 M NaF and NaCl. In this concentration range the difference dielectric permittivity and loss were found to be almost proportional to the salt concentration, indicating that hydrated solutes are dispersed in the bulk water. It justifies adopting the Hanai mixture theory. Thus, the dielectric spectra of NaCl and NaF solutions were decomposed into hydrated solutes and bulk water. The dielectric spectra of spherical solutes with a water layer at given ϕ ($\geq \phi_B$) were then successfully decomposed into a few Debye functions and the bulk component, where ϕ_B is defined as the volume fraction of hydrated solute when $\alpha = 0$. The relaxation frequencies f_{c_1} of the hypermobile component for NaF and NaCl solutions were in the range of 18−20 GHz. The present results indicate that the spectra of NaCl solutions at $\phi = \phi_B$ were simulated with single Debye relaxation function above 3 GHz, as opposed to our expectation that at least two Debye functions must be required corresponding to individual hydration shells of anion and cation. It may be related to solvent-shared ion-pair or solvent-separated ion pair dispersed in bulk water.[11,17]

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