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Dielectric Relaxation Behavior of Glycine Betaine in Aqueous Solution

Toshiyuki Shikata*

Department of Macromolecular Science, Osaka University, Toyonaka, Osaka 560-0043, Japan

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Dielectric relaxation behavior of aqueous glycine betaine (*N*,*N*,*N*-trimethylglycine) (GB) solutions was examined as a function of frequency from 6.28×10^6 to 1.26×10^{11} rad s^{-1} (1.00×10^6 to 20.0×10^9 Hz). Two kinds of relaxation modes were observed at frequencies of 1.25×10^{11} and 2.5×10^{10} rad s^{-1}. The fast relaxation mode of which strength decreases with increasing the concentration of GB corresponds to the rotational relaxation mode of the medium, water. The other mode has relaxation strength proportional to the concentration of GB and is attributed to the rotational relaxation mode of GB bearing hydrated water molecules. To evaluate the magnitude of dipole moment (μ) and the number of tightly hydrated water molecules (m) to GB in aqueous solution, an analytical model proposed previously was employed, then, the values, $\mu \sim 8.0$ D and $m = 2$, were evaluated irrespective of the concentration of GB. On the other hand, ab initio quantum chemical calculations were carried out to determine the magnitude of μ for GB dihydrate as a model describing the state of GB in an aqueous solution. Agreement between the μ values obtained from experimental results and the calculation is reasonably good.

Introduction

Zwitterionic compounds possess high solubility in water, and they still have bipolar structure keeping relatively long separation between two opposite charges even in aqueous solution. Thus, it is anticipated that zwitterions have considerably large dipole moments in an aqueous solution, e.g., greater than 10 D. However, reliable data and discussion on the dipole moments had not been reported for zwitterions and other polar solute molecules with relatively large dipole moments in solutions of polar solvents such as water.[1] We do not have a general method to evaluate the magnitude of dipole moments for polar solutes in aqueous solutions, although well-known Debye's method[2−4] is very useful in dilute solutions of polar solutes in nonpolar media. Of course, it is important to establish a general method that can provide the precise value of dipole moments for polar solutes in solution of polar solvents through data obtained by conventional dielectric relaxation measurements.

We recently proposed a method for estimation of values of dipole moments for polar solutes in solutions of polar solvents.[5,6] The method was applied to results of dielectric relaxation measurements for aqueous solutions of a polar molecule, trimethylamineoxide (TMAO).[6] The calculated value of a dipole moment (μ) for TMAO was 4.2 D, and the evaluated number of tightly hydrated water molecules (m) to TMAO was two. These values look plausible because TMAO is a molecule which develops strong hydrogen bonding between water molecules to form air stable crystals with dihydrate structure.[7] Ab initio quantum chemical calculations provide the value of μ for TMAO hydrates depending on the value of m. Since TMAO dihydrate might be a model describing the state of TMAO in an aqueous solution, making a comparison between the magnitude of μ calculated from experimental results and that obtained by the ab initio calculation is one of ways to confirm the validity of the proposed method.

In this study, the dielectric behavior of aqueous solution of a simple zwitterion, glycine betaine (*N*,*N*,*N*-trimethylglycine)(GB), was examined as a function of frequency from 6.28×10^6 to 1.26×10^{11} rad s^{-1} (1.00×10^6 to 20.0×10^9 Hz). From the estimated relaxation time, the size of GB in aqueous solution is discussed, moreover, the values of μ and m for GB in aqueous solution is calculated by using the analytical method which we have proposed.[5,6] Furthermore, ab initio quantum chemical calculations were performed to calculate the values of μ and m for GB in aqueous solution. A comparison between the magnitude of μ obtained from experiments and that from the ab initio calculation makes clear that the analytical method proposed is valid and general for the evaluation of μ for polar solute molecules such as GB in solution of polar solvents.

Because zwitterionic groups such as dimethylammonio acetate are typical hydrophilic headgroups for betaine type surfactants such as (dodecyldimethylammonio)acetate, investigating the dielectric behavior of zwitterions leads to understanding the mechanism of micelle formation and micro-dynamics in micelles for betaine type surfactants. Moreover, GB and TMAO are widely occurring in nature. They accumulate within some biological cells up to very high concentration, and work as osmotic pressure controller to cope with water stress.[8] Therefore, the investigation of dielectric behavior for these substances in aqueous solution will make a key step forward full understanding of a biological mechanism to control the condition of living.[9]

Experimental Section

Materials. Glycine betaine, GB, was purchased from Wako pure chemical Industries, Ltd.(Osaka) in anhydrous structure and was used without any further purification. Highly deionized water with the specific resistance higher than 16 MΩcm obtained by a Milli Q system (Nihon MilliPore, Tokyo) was used as a solvent. The concentration (c) of GB was ranged from 100 to 1000 mM.

Methods. Dielectric relaxation measurements were performed using two kinds of systems depending on measurement frequen-

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* To whom correspondence should be addressed. E-mail: shikata@chem.sci.osaka-u.ac.jp. Fax: + 81-6-6850-5538.

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cies (ω). A system which is consisting of an RF LCR meter (4287A, Agilent Technologies Japan, Tokyo) and a homemade electrode cell with the vacant capacitance (C_0) of 0.23 pF was used in the ω range from 6.28×10^6 to 6.28×10^9 rad s^{-1} (1×10^6 to 1×10^9 Hz). In an ω range from 6.28×10^8 to 1.26×10^{11} rad s^{-1} (100×10^6 to 20×10^9 Hz), a dielectric material probe system (HP85070B, Hewlett-Packard) composed of a network analyzer (HP8720ES, Hewlett-Packard) and a coaxial probe cable was operated. In both systems, the sample temperature was kept constant at 25 °C by circulating thermostated water. The detailed measurement procedure was reported elsewhere.[10,11] The real and imaginary parts (ϵ' and ϵ'') of complex permittivity ($\epsilon^* = \epsilon' - \mathrm{i}\,\epsilon''$) for sample liquids were estimated as functions of ω in both systems.

Density measurements for sample solutions were performed using a density meter (DMA 5000, Anton Paar, Graz) at 25 °C to evaluate the specific volume of GB in aqueous solution.

Ab Initio Calculations. Ab initio quantum chemical calculations were performed with Gaussian 98[12] to evaluate optimized geometries and the values of μ for tightly hydrated GB in aqueous solution as a function of the number of hydrated water molecules, m. We have employed the basis set of 6-31G** which has been widely used and recommended for quantitative quantum chemical calculations.[13]

Geometry optimization was performed with conventional Hartree–Fock (HF) theory and also with a Møller–Plesset perturbation theory[14] (MP2) including electron correlation contribution by second order. The initial positions of water molecules for GB monohydrate and dihydrate were preliminarily determined by semiempirical quantum chemical calculations with a potential function, PM3, on Guassian 98. The heat of hydrogen bond formation was calculated for each optimized geometry using a counterpoise method[15] that can correct effectively the basis set superposition error (BSSE). All calculations were carried out on a computer system in Ueyama's laboratory, Department of Macromolecular Science, Osaka University. Pictures of determined optimized geometries were generated by freely available software, Prax.[16]

Results

Dielectric Spectra for Aqueous GB Solutions. Dielectric spectra of GB in aqueous solution ($\Delta\epsilon'$ and $\Delta\epsilon''$) are evaluated in the form of differences from those of pure water; $\Delta\epsilon' = \epsilon' - f\epsilon_{\mathrm{w}}'$ and $\Delta\epsilon'' = \epsilon'' - f\epsilon_{\mathrm{w}}''$, 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. The value of f was determined as a function of c supposing that GB has no dielectric relaxation modes in a high ω region close to the relaxation frequency of pure water molecules ($\omega_{\mathrm{w}} = 1.25 \times 10^{11}$ rad s^{-1}). Figure 1 show the dependencies of $\Delta\epsilon'$, $\Delta\epsilon''$, ϵ', ϵ'', $f\epsilon_{\mathrm{w}}'$, and $f\epsilon_{\mathrm{w}}''$ on ω for an aqueous GB solution at 1000 mM on the assumption of $f = 0.82$ as typical results.

In general, dielectric spectra can be described by the summation of Debye type relaxation functions with some sets of a relaxation time and strength. However, in the aqueous GB solutions, $\Delta\epsilon'$ and $\Delta\epsilon''$ are well described with only one set of a relaxation time and strength (τ and $\Delta\epsilon$) as given below:

$$\Delta\epsilon' = \Delta\epsilon/(1 + \tau^2\omega^2) \tag{1a}$$

$$\Delta\epsilon'' = \Delta\epsilon\tau\omega/(1 + \tau^2\omega^2) \tag{1b}$$

Solid lines in Figure 1 for $\Delta\epsilon'$ and $\Delta\epsilon''$ represent the best fit curves calculated with eqs 1a and 1b. The values of $f = 0.82 \pm 1$ produce $\Delta\epsilon'$ and $\Delta\epsilon''$ spectra well described by the Debye type relaxation functions with $\tau = 4.0 \times 10^{-11}$ s and $\Delta\epsilon = 32$. Because the ω dependence of the obtained $\Delta\epsilon'$ spectrum highly depends on the f value especially in the high ω region close to ω_{w}, the f value can be determined as the obtained $\Delta\epsilon'$ spectrum decreases with a slope of -2.0 in a double-logarithmic plot as seen in Figure 1. Thus, the value of f is determined keeping an error less than 3%.

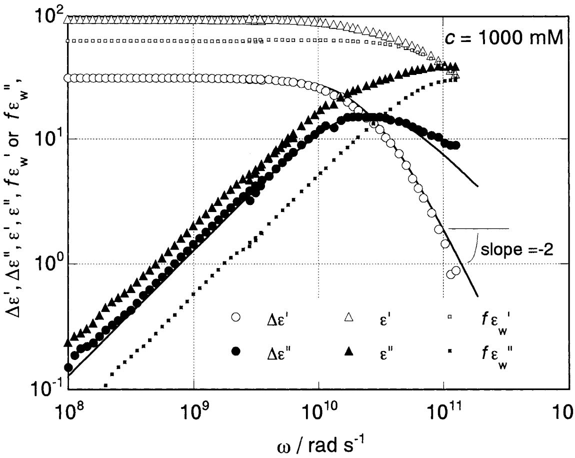

Figure 1. Frequency (ω) dependencies of dielectric spectra, $\Delta\epsilon'$, $\Delta\epsilon''$, ϵ', ϵ'', $f\epsilon_{\mathrm{w}}'$, and $f\epsilon_{\mathrm{w}}''$, for an aqueous glycine betaine (GB) solution at the concentration (c) of 1000 mM. The value of $f = 0.82$ is assumed.

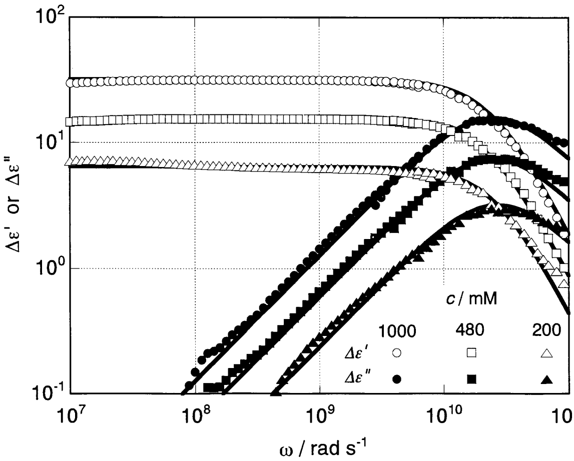

Figure 2. Dependencies of $\Delta\epsilon'$ and $\Delta\epsilon''$on ω for aqueous GB solutions with several concentrations at 25 °C. Solid lines represent the best fit curves obtained by Debye type relaxation functions, eqs 1a and 1b.

Consequently, the dielectric spectra, ϵ' and ϵ'', of aqueous GB solutions possess two relaxation modes. The fast mode found at ω_{w} is assigned to the rotational relaxation of water molecules. The other mode possessing parameters, τ and $\Delta\epsilon$, is the contribution of the presence of GB molecules.

The dependencies of dielectric spectra, $\Delta\epsilon'$ and $\Delta\epsilon''$, on ω for some aqueous GB solutions are plotted in Figure 2. Solid lines in Figure 2 represent calculated spectra with eqs 1a and 1b, which are the best fit curves for the data shown.

Fitting parameters, τ and $\Delta\epsilon$, used for the obtained best fit curves are shown in Figure 3 parts a and b, respectively, as functions of c. It is likely that the value of τ, which should correspond to the rotational relaxation time of GB in aqueous solution, is independent of c. The equivalent rigid sphere radius (r_{e}) of GB in aqueous solution can be estimated using the relationship of $\tau = 4\pi r_{\mathrm{e}}^3\eta/(k_{\mathrm{B}}T)$; where η and $k_{\mathrm{B}}T$ represent the viscosity of medium water at 25 °C and the product between Boltzmann's constant and the absolute temperature. Then, we

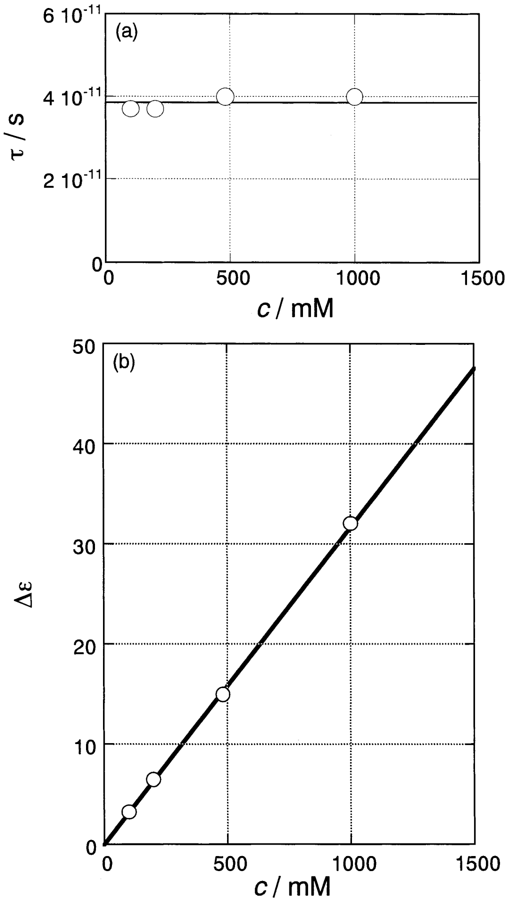

Figure 3. (a) Dependence of dielectric relaxation times (τ) on the concentration of GB (c) for aqueous GB solutions at 25 °C. (b) Relationship between dielectric relaxation strength ($\Delta\epsilon$) and c for the same aqueous solutions.

obtain $r_e = 0.23$ nm which is smaller than the value of average radius (r_m) estimated from the specific molar volume ($v_m = 99.2$ cm^3 mol^{-1}) of GB in aqueous solution by 0.11 nm. The reason for this discrepancy might be that water molecules surrounding GB molecules do not behave as a continuous medium possessing constant η at the frequency range discussed. Such a discrepancy between r_e and r_m was also observed in aqueous solutions of TMAO.[6]

The value of $\Delta\epsilon$ is perfectly proportional to c as seen in Figure 3b. A slope between $\Delta\epsilon$ and c is estimated to be 33.3 M^{-1} and will be used later to evaluate the magnitude of dipole moment, μ, for GB in aqueous solution. The proportionality observed in Figure 3b strongly suggests that there exists no special interaction such as intermolecular association formation between GB molecules which dramatically reduces or enhances the total magnitude of polarization for the solutions in the c range examined.

Figure 4 shows the relationship between the value of f and c including experimental errors for the aqueous GB solutions. A solid line represents the volume effect of the solute, GB, on f estimated by an equation below proposed by Pottel et al.;[17] $v = c\ v_m$:

$$f = (1 - v)/[1 + (1/2)v] \qquad (2)$$

It is well-known eq 2 describes the c dependence of f in a case that a solute molecule has no tightly hydrated water molecules on their surface.[6] However, if the solute has m of tightly hydrated water molecules which are dead, in other words, saturated dielectrically in an ω range lower than 10^{11} rads^{-1}, an additional factor of $-mc/55.6$ to correct the contribution of tightly hydrated water molecules is necessary.[5,6] Dash, chain, and dotted lines represent calculated c dependence of f with $m = 1$, 2, and 3, respectively. Agreement between the data of f for the aqueous GB solution and a calculated curve using $m = 2$ looks reasonable.

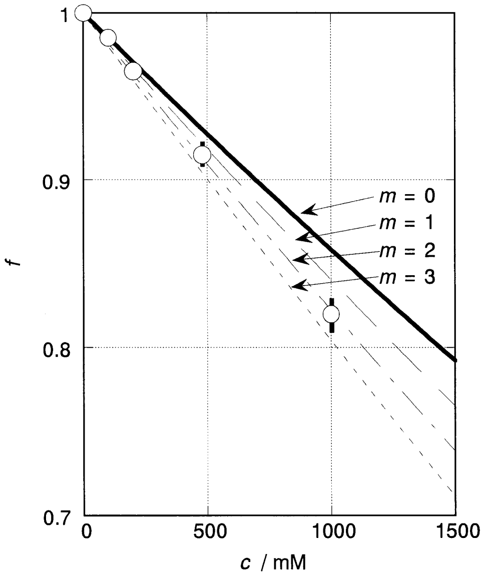

Figure 4. Relationship between the fraction contribution of water molecules (f) to the dielectric relaxation behavior and the concentration, c, for aqueous GB solutions at 25 °C.

From these, we can summarize shortly characteristics of dielectric behavior for GB in aqueous solution as follows. GB is tightly hydrated by two water molecules in aqueous solution, and it keeps a rotational relaxation mode with the relaxation time, τ, which is much longer than that of water molecules in the bulk state.

Ab Initio Calculations. Optimized geometrical parameters and the magnitude of μ for GB obtained at HF/6-31G** and MP2/6-31G** level are summarized in Table 1. The optimized geometry of GB obtained at HF/6-31G** level is shown in Figure 5i. The other optimized geometry of GB by MP2 theory is very similar to that by HF theory and also to the experimental data obtained by a X-ray diffraction technique.[18] The magnitudes of μ for the optimized geometries by both theories are completely identical with 11.9 D. These imply that both theories, HF and MP2, provide reasonably realistic optimized geometries with the 6-31G** basis set for GB. Very recently, Sironi et al.[19] also calculated the optimized structural parameters for GB at the same HF/6-31G** level and obtained the same result.

The optimized geometry of GB monohydrate obtained by HF theory is shown in Figure 5ii. Most of geometrical parameters for GB except for the torsion angle of carboxyl group, τO1−CA−C3−N, are not so much altered by the presence of a tightly hydrated water molecule. The total magnitude of μ for GB monohydrate is considerably reduced to 10.6 D because of the effective orientation of the tightly hydrated water molecule. More dramatic reduction in the total magnitude of μ to 8.6 and 8.3 D happens to GB dihydrate as seen in the optimized geometries determined by HF theory (Figure 5 parts iii and iv). Actually, preliminary semiempirical quantum chemical calculations predict two possible initial positions for the second water molecule of GB dihydrate. Then, we find two possible optimized geometries for GB dihydrate via ab initio quantum chemical calculations at HF/6-31G** level. In both the optimized

TABLE 1: Optimized Geometrical Parameters and the Magnitude of μ for GB Obtained at the HF/6-31G and MP2/6-31G** Levels**

parameters[a]		HF/6-31G** (i)	MP2/6-31G** (v)
λO1-CA	0.1 nm	1.213	1.242
λO2−CA	0.1 nm	1.231	1.264
λCA-C3	0.1 nm	1.572	1.579
λH7−C3	0.1 nm	1.081	1.089
λH8−C3	0.1 nm	1.081	1.089
λC3−N	0.1 nm	1.518	1.522
λH1−C1	0.1 nm	1.082	1.087
λH2−C1	0.1 nm	1.076	1.087
λH3−C1	0.1 nm	1.081	1.086
λC1−N	0.1 nm	1.494	1.497
λH4−C2	0.1 nm	1.082	1.088
λH5−C2	0.1 nm	1.080	1.086
λH6−C2	0.1 nm	1.080	1.086
λC2−N	0.1 nm	1.483	1.498
αO1−CA-O2	deg	133.0	133.2
αO1−CA-C3	deg	110.2	109.9
αH7−C3−N	deg	106.7	106.2
αH7−C3−H8	deg	108.5	108.9
αCA-C3−N	deg	117.1	116.5
αH1−C1−H2	deg	111.8	110.3
αH3−C1−H1	deg	109.7	112.7
αH1−C1−N	deg	108.6	108.4
αH4−C2−H5	deg	109.7	110.2
αH6−C2−H4	deg	109.7	109.9
αH4−C2−N	deg	109.4	109.2
τO1−CA-C3−N/deg	0.0	0.0	0.0
τCA-C3−N−C2/deg	180.0	180.0	180.0
τH7−C3−N−C1	deg	177.5	177.9
τH1−C1−N−C3	deg	179.1	179.5
τH4−C2−N−C3	deg	180.0	180.0
$\boldsymbol{\mu}$	Debye	11.9	11.9

[a] λ, distance; α, triangular angle; τ, dihedral angle; cf. Figure 5 for atomic description.

geometries, the second water molecule hydrates to GB forming hydrogen bonding to the other oxygen atom, O2, of the carboxyl group keeping very effective orientation to reduce the total magnitude of μ as seen in the figure. The second water molecule of the geometry in Figure 5iii is placed on the same side of the carboxyl group relative to the first water molecule. However, the second water molecule of the other optimized geometry shown in Figure 5iv is placed at a position near a plane which is formed by two oxygen atoms of the carboxyl group and the oxygen atom of the first water.

The optimized geometrical parameters, the heat of hydrogen bond formation (ΔH_{hyd}) and the total magnitude of μ for GB monohydrate and dihydrate determined by HF theory are summarized in Table 2. The value of ΔH_{hyd} for GB dihydrate means that for the second hydrated water molecule. Because the absolute value of ΔH_{hyd} for the second water molecule of the geometry seen in Figure 5iii is very close to that of the geometry in Figure 5iv, we are not able to determine which geometry is more convincing.

Because preliminary semiempirical quantum chemical calculations also predict the possibility of GB trihydrate, we tried to find the optimized geometry for GB trihydrate. However, because the conversion of displacement for atoms was not successful, the optimized geometry for GB trihydrate was not determined even by using the simple HF theory.

The optimized geometries for GB monohydrate and dihydrate determined at the MP2/6-31G** level are shown in Figure 5 parts v and vi, respectively. In the case of the calculation at the MP2/6-31G** level, we can find only one optimized geometry for GB dihydrate in contrast with the result obtained at HF/6-31G** level. The geometries are not only similar to those in Figure 5 parts ii and 5iv but also the values of μ for GB monohydrate and dihydrate are reasonably close to those determined at HF/6-31G** level as summarized in Table 2. The fact that the absolute values of ΔH_{hyd} determined at the MP2/6-31G** level are obviously greater than those obtained at the HF/6-31G** level suggests the optimized geometries in Figure 5 parts v and vi are more realistic than those in Figure 5 parts ii and iv. Although the MP2 theory takes account of the contribution of electron correlation by second order, the HF theory does not include such the contribution. Then, it is likely that the results obtained at the MP2/6-31G** level are more realistic than those obtained at the other level. Nevertheless, disagreement in the values of geometrical parameters, μ, and also ΔH_{hyd} determined at these levels is relatively small. Thus, we believe that the optimized geometries for GB dihydrate (Figure 5 parts iv and vi) are close to the real geometries of GB tightly hydrated by two water molecules in aqueous solution.

The magnitude of absolute values of ΔH_{hyd} for the first and second water molecules is in a range from 8 to 10 kcal mol^{-1} and is close to that for a water molecule hydrated to TMAO.[6] Thus, we may conclude that GB can be easily and tightly hydrated by two water molecules in aqueous solution and the total magnitude of μ for GB hydrates is effectively reduced to the value of 8.1~8.3 D, which is much less than that observed in the bare GB molecule.

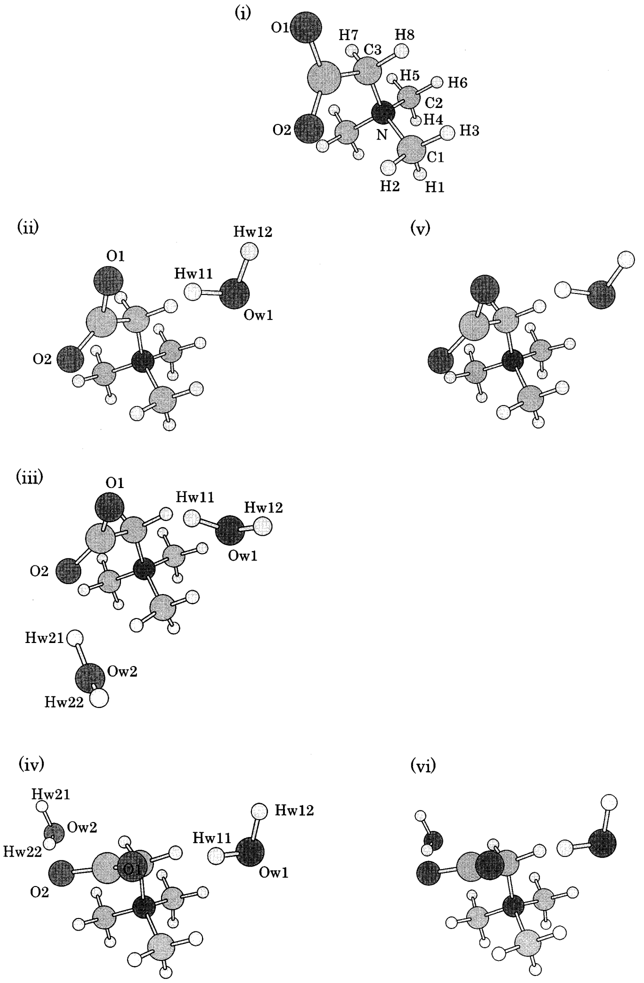

Figure 5. Optimized geometries for GB and GB hydrates determined by ab initio quantum chemical calculations. (i) GB obtained at the HF/6-31G** level; (ii) GB monohydrate at the HF/6-31G** level; (iii) and (iv) GB dihydrate at the HF/6-31G** level; (v) GB monohydrate at the MP2/6-31G** level; and (vi) GB dihydrate at the MP2/6-31G** level.

TABLE 2: Optimized Geometrical Parameters, Magnitude of μ, and Heat of Hydrogen Bond Formation (ΔH_{hyd}) for GB Monohydrate and Dihydrate Determined at the HF/6-31G and MP2/6-31G** Levels**

GB Monohydrate

parameters[a]		HF/6-31G** (ii)	MP2/6-31G** (v)
λO1−CA	0.1 nm	1.225	1.258
λO2−CA	0.1 nm	1.225	1.257
λCA-C3	0.1 nm	1.564	1.566
αO1−CA-O2	deg	131.5	131.1
αO1−CA-C3	deg	111.3	112.1
τO1−CA-C3−N	deg	156.9	148.8
τCA-C3−N−C2	deg	−172.5	−167.7
λOw1-O1	0.1 nm	2.835	2.763
αOw1-O1−CA	deg	100.4	101.4
αOw1-Hw11-O1	deg	157.3	164.9
τOw1-O1−CA-C3	deg	−56.2	−44.6
τHw12-Ow1-O1−CA	deg	149.9	165.8
λHw11-Ow1	0.1 nm	0.950	0.981
λHw12-Ow1	0.1 nm	0.940	0.962
αHw11-Ow1-Hw12	deg	103.8	103.9
μ	Debye	10.6	10.2
ΔH_{hyd}	kcal mol^{-1}	−8.76	−10.32

GB Dihydrate

parameters[a]		HF/6-31G** (iii)	HF/6-31G** (iv)	MP2/6-31G** (vi)
λO1−CA	0.1 nm	1.224	1.225	1.259
λO2−CA	0.1 nm	1.230	1.233	1.267
λCA-C3	0.1 nm	1.555	1.557	1.554
αO1−CA-O2	deg	130.3	129.9	129.1
αO1−CA-C3	deg	113.2	114.9	115.4
τO1−CA-C3−N	deg	142.8	105.3	101.4
τCA-C3−N−C2	deg	−166.9	−170.3	−169.4
λOw1-O1	0.1 nm	2.814	2.819	2.753
αOw1-C1−CA	deg	100.0	113.3	110.2
αOw1-Hw11-O1	deg	160.7	159.8	163.4
τOw1-O1−CA-C3	deg	−53.4	1.47	5.70
τHw12-Ow1-O1−CA	deg	−151.1	94.4	92.3
λHw11-Ow1	0.1 nm	0.960	0.957	0.984
λHw12-Ow1	0.1 nm	0.940	0.943	0.963
αHw11-Ow1-Hw12	deg	106.4	105.6	104.1
λOw2-O2	0.1 nm	2.820	2.816	2.747
αOw2-C2−CA	deg	110.0	109.3	106.9
αOw2-Hw21-O1	deg	146.2	161.4	165.9
τOw2-O2−CA-C3	deg	108.7	−29.3	−26.4
τHw22-Ow2-O2−CA	deg	50.2	−98.2	−102.0
λHw21-Ow2	0.1 nm	0.950	0.957	0.983
λHw22-Ow2	0.1 nm	0.940	0.942	0.962
αHw21-Ow2-Hw22	deg	107.5	106.4	104.3
μ	Debye	8.6	8.3	8.1
ΔH_{hyd}	kcal mol^{-1}	−7.55	−7.50	−9.02

[a] λ, distance; α, triangular angle; τ, dihedral angle; cf. Figure 5 for atomic description.

Sironi et al.[19] performed molecular dynamics simulations for water molecules around GB to calculate spatial distribution of them and to identify where hydrogen bonding occurs between GB and them. They simulated the distribution of water molecules around GB at fixed structural parameters determined for the individual or bare GB molecule. However, it is clear that the torsion angle of a carboxyl group of GB is influenced by the presence of tightly hydrated water molecules as seen in Figure 5 parts ii−vi. Sironi et al.[19] also discussed the rates of rotation of some functional groups about chemical bonds and reported the rotational rate of the carboxyl group is on the order of 10^{10} s^{-1}. It should be possible that the rotational rate is considerably reduced by the presence of the tightly hydrated water molecules to GB.

Discussion

Calculation of μ for GB from Dielectric Data. According to a model[5,6] which has been proposed previously, the concentration reduced dielectric relaxation strength, $\Delta\epsilon c^{-1}$, for a solute, GB, is proportional to the square of μ as given by eq 3, where A, N_A, and ϵ_v represent a factor defined by eq 4, Avogadoro's number, and the permittivity of a vacuum, respectively.:

$$\Delta\epsilon c^{-1} = AN_A\mu^2/(2\epsilon_v kT) \qquad (3)$$

$$A = 1 + \mu_w\mu^{-1}z\cos\gamma \qquad (4)$$

where μ_w, z, and γ represent the dipole moment of a water molecule (ca. 1.95 D), the number of the first neighbor water molecules surrounding tightly hydrated GB, and the average angle between the total dipole of tightly hydrated GB and dipoles of the first neighbor water molecules.

The value of z can be roughly calculated from the average radius of GB, r_m = 0.34 nm, evaluated by the specific molar volume, v_m, of GB in aqueous solution in the manner; $z = (4\pi/3)\{(r_m + 2r_w)^3 - r_m^3\}\rho_w \sim 31$, 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.

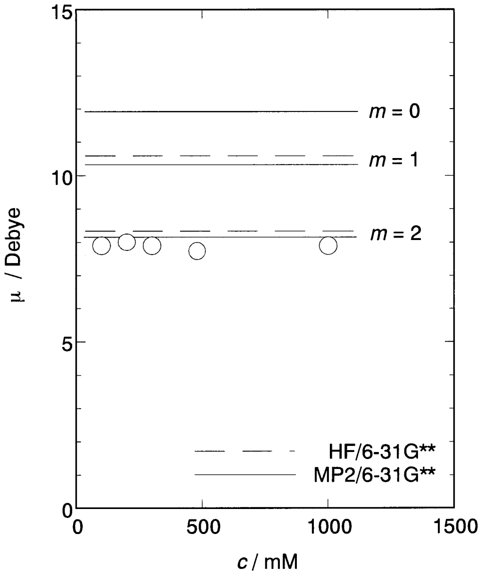

Figure 6. Dependence of the magnitude of dipole moment (μ) for GB on c in aqueous solution at 25 °C. Solid and broken lines respectively represent the obtained values by ab initio quantum chemical calculations at the MP2/6-31G** and HF/6-31G** levels as function of the number of tightly hydrated water molecules (m) to GB.

3.35×10^{22} cm^{-3} at 25 °C). Sironi et al.[19] reported the value of $z + m$ to be ~25 by means of the spatial distribution function of water molecules around a GB molecule obtained by molecular dynamics simulations. However, this value is smaller than the value calculated above by 24%. In their paper, they showed the radial distribution function of water oxygen atoms ($g(r)$) around the nitrogen atom of GB as a function of distance (r).[19] The magnitude of $g(r)$ starts increasing at $r = 0.35$ nm $\sim r_m$ and shows a maximum at $r = 0.45$ nm $\sim r_m + r_w$ and is followed by decreasing to show a shallow minimum at $r = 0.62$ nm $\sim r_m + 2r_w$.[19] Because a nitrogen atom is placed at almost the geometrical center of GB, one can estimate the value of $z + m$ by a numerical integration process of $g(r)$ up to $r = 0.62$ nm. The result of the integration gives $z + m = 31$, and the value is close to that obtained above. From these, here we adopt the value of 31 as z. Moreover, although Sironi et al.[19] evaluated m to be seven via the result of their molecular dynamics simulation supposing a quite mild definition of hydrogen bond formation, the value of seven should be considerably overestimated.

The value of z for TMAO[6] calculated from the value of v_m is 30 and is identical well with the value estimated by the spatial distribution function of water oxygen atoms evaluated by the molecular dynamics simulation.[20] Because the value of γ for TMAO, which is similar to GB in size and chemical structure, is about 53° in aqueous solution, the value of γ for aqueous GB solution is assumed to be identical with the value. Then, eq 4 is rewritten as eq 5, and the value of μ can be evaluated by applying eq 3 to the experimental data, $\Delta\epsilon c^{-1}$, shown in Figure 3b:

$$A = 1 + 36.4\mu^{-1} \tag{5}$$

The determined μ value for hydrated GB hydrates are plotted as a function of c in Figure 6.

The experimentally calculated μ values for GB via the analytical method look independent of c and are less than the values obtained using the ab initio quantum chemical calculation for its bare state. In Figure 6, the total magnitudes of μ for GB hydrates evaluated by using HF and MP2 theories are also shown with solid and broken lines. The agreement between the magnitude of μ calculated from experimental results (~ 8.0 D) and the total magnitude of μ calculated by the ab initio method for $m = 2$ is reasonably good. Because the experimentally determined m for aqueous GB solutions is 2 as described above (Figure 4), this agreement in the magnitude of μ suggests that the analytical method successfully works, and GB is tightly hydrated by two water molecules in aqueous solution.

Conclusion

Dielectric relaxation behavior of aqueous GB solutions has two relaxation modes at frequencies of 1.25×10^{11} and 2.5×10^{10} rad s^{-1}. The fast relaxation mode is assigned to the rotational relaxation mode of pure water. The slow mode of which relaxation strength is proportional to the concentration of GB is attributed to the rotational relaxation mode of GB tightly hydrated by some water molecules. To evaluate the magnitude of dipole moment (μ) and the number of water molecules (m) tightly hydrated to GB in the solution, a proposed analytical method was used, and then the values of $\mu \sim 8.0$ D and $m = 2$ were obtained irrespective of the concentration of GB. Ab initio quantum chemical calculations evaluate the magnitude of μ as a function of m for GB. Reasonable agreement between the μ value calculated from experimental results and that obtained by the ab initio calculation suggests the analytical method works successfully in polar solutions to evaluate μ of polar solute molecules such as GB.

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