Hydration Structure and Dynamic Behavior of Poly(vinyl alcohol)s in Aqueous Solution

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ABSTRACT: High-frequency dielectric relaxation measurements up to 20 GHz were conducted in aqueous solutions of poly(vinyl alcohol)s (PVAs) to examine their hydration structures and dynamic behavior. Dielectric relaxation spectra of aqueous PVA solutions decomposed well into three sets of the Debye-type relaxation modes. This was attributed to the rotational relaxation mode of free water molecules, an exchange mode of water molecules hydrated to hydroxy (OH) groups for bulk water, and local motions of PVA main chains. OH groups of PVAs keep ca. 2−2.2 hydrated water molecules in aqueous solution, in contrast to the hydration behavior of 1,4-cyclohexanedimethanol and 1,4-cyclohexanediol model molecules possessing OH groups that lack intramolecular hydrogen bond formation, which keep ca. 5 water molecules per OH group in aqueous solution. In the case of PVAs, the formation of intramolecular hydrogen bonding between mainly adjacent OH groups effectively diminishes their hydration numbers.

Introduction

Poly(vinyl alcohol) (PVA), a typical synthetic water-soluble polymer possessing one hydroxyl (OH) group per monomer, was first synthesized by Herrmann and Haehnel[1] in 1924. Since then, studies on basic physicochemical properties of PVAs both in the bulk state and in solution have been carried out widely by means of various techniques.[2–5] Generally, the physicochemical properties of water-soluble polymers in aqueous or mixed aqueous solution depend highly on the strength of interactions between water molecules and hydrophilic moieties in the polymers, such as hydrogen bonds. In the case of PVAs, the formation of inter- and intramolecular hydrogen bonds between OH groups belonging to monomer units also influences their solution properties. Takigawa et al.[6,7] investigated the critical behavior of the specific and intrinsic viscosity of PVA solutions in the vicinity of gelation points and showed that intramolecular hydrogen bond formation made the conformation of PVA molecules compact in a low concentration region. Cheng et al.[8,9] repeated a freezing−thawing treatment several times in PVA solutions and claimed the dominance of intramolecular hydrogen bonds in a dilute region. An atomic force microscopy (AFM) observation[10] revealed that the hydrogen bonds govern the elastic properties of PVAs and form the multiple-stranded structure of PVAs in aqueous solution. An NMR study of some model compounds for PVA revealed that the intramolecular hydrogen bonds stabilize the conformations of PVA.[11] Dynamics of polymer chains and solvent molecules relevant to polymer–polymer and polymer–water interactions in aqueous PVA systems have been investigated by dielectric relaxation measurements[12–14] and molecular dynamics simulation studies.[15–19]

It is likely that the hydration state and dynamics of PVA molecules in aqueous solution are highly dependent on the formation of inter- or intramolecular hydrogen bonds between OH groups. However, the relationship between these bonds has not yet been discussed in detail.

The dielectric relaxation (DR) measurement is a powerful method for detecting the presence of electric dipoles in measured systems and provides information about the dynamics of the dipoles. A hyper-high-frequency DR method up to some tens of gigahertz, which corresponds to the rotational relaxation frequency of liquid water molecules possessing relatively large dipole moment of 1.85 D, provides us with significant information about hydration and dynamics of the solutes and also solvent molecules in aqueous and polar media.[20–24]

In the present study, we performed hyper-high-frequency DR measurements for aqueous solutions of PVAs with different degrees of polymerization, n, to investigate the hydration structure and dynamic behavior of PVAs in aqueous solution. The DR behavior of aqueous solutions of low molar mass model compounds, such as 1,4-cyclohexanedimethanol (CHDM) and 1,4-cyclohexanediol (CHDO), possessing OH groups without intramolecular hydrogen bond formation, was also investigated to confirm the effect of intramolecular hydrogen bond formation on the hydration behavior of PVA OH groups.

Experimental Section

Materials. PVAs with particular degrees of polymerization, n, of 1000 and 2000 (PVA-1000 and PVA-2000, respectively) were kindly supplied by Japan VAM & Poval Co., Ltd. (Sakai, Japan). CHDM and CHDO were purchased from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan) and Aldrich (Milwaukee, WI), respectively. Highly deionized water with a specific resistance higher than 15 MΩ cm was obtained by an Elix-UV3 system of Nippon Millipore K. K. (Tokyo, Japan) and was used as a solvent for sample preparations. The concentrations, c_P, of the PVAs ranged from 0.5 to 2.1 M in monomer units, and the concentrations, c, of the CHDM and CHDO ranged from 0.5 to 1.7 M. Deuterium oxide (D_2O) with a purity of 99.9% was purchased from Cambridge Isotope Laboratories, Inc. (Andover, MA) as a solvent for ^{13}C NMR measurements. The c_P of PVA-2000 in D_2O solution for ^{13}C NMR measurements was 2.2 M.

Methods. Dielectric relaxation measurements were conducted over an angular frequency, ω, ranging from 6.28×10^6 to 1.26×10^{11} rad s^{-1} (1.0×10^6 to 2.0×10^{10} Hz), using two types of systems at 25 °C. A lower ω range from 6.28×10^6 to 1.88×10^{10} rad s^{-1} was covered by an RF LCR meter (Agilent Technologies, 4287A) equipped with a homemade electrode cell with the vacant capacitance, C_0, of ca. 0.23 pF. The real and imaginary parts, ϵ' and ϵ'', of the complex permittivity were evaluated by the conventional formulas of $\epsilon' = CC_0^{-1}$ and $\epsilon'' = (G - G_{dc})C_0^{-1}\omega^{-1}$, where C, G, and G_{dc} are the capacitance of the electrode cell filled with samples, the conductivity of the samples, and the direct current conductivity due to ionic impurities, respectively. A dielectric material probe system (Hewlett-Packard, 85070C) consisting of a network analyzer

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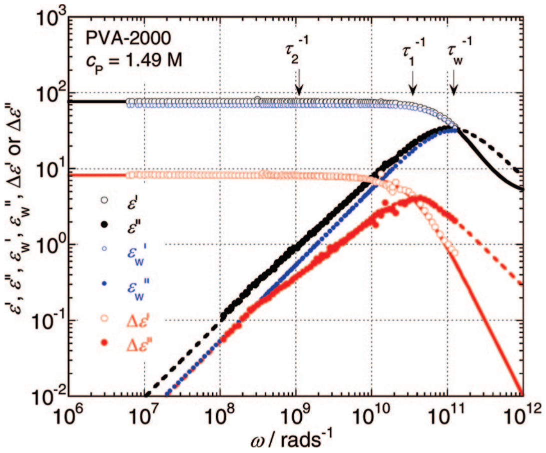

Figure 1. Dependence of ϵ' and ϵ'' on ω, the so-called dielectric spectra, for an aqueous solution of PVA-2000 at $c_P = 1.49$ M and 25 °C. Dielectric spectra for bulk state water in the solution, ϵ_w' and ϵ_w'', and differential dielectric spectra for the solution, $\Delta\epsilon' = \epsilon' - \epsilon_\infty - \epsilon_w/(1 + \omega^2\tau_w^2)$ and $\Delta\epsilon'' = \epsilon'' - \epsilon_w\omega\tau_w/(1 + \omega^2\tau_w^2)$ showing the essential contribution of the solute PVA, are also plotted. Solid and broken lines represent fitted spectra for the solution and differential spectra calculated via eq 1 with parameters summarized in Table 1.

(Hewlett-Packard, 8720ES) was employed in the ω range of $3.14 \times 10^8 - 1.26 \times 10^{11}$ rad s^{-1}. Details of the measurement procedures are described elsewhere.[25]

To determine the partial (monomer unit) molar volumes ($\bar{V}_m$) of PVAs, CHDM, and CHDO in aqueous solution, the densities of the aqueous solutions were measured at 25.0 °C using an Anton Paar DMA5000 digital density meter (Graz, Austria).

Longitudinal relaxation times (T_1) of ^{13}C NMR for a D_2O solution of PVA-2000 at different resonance frequencies were determined at 30 °C using a Varian UNITY plus 600-NMR spectrometer (resonance frequency for ^{13}C, $\omega_r = 150.8$ MHz) and a JEOL EX-270 spectrometer ($\omega_r = 67.80$ MHz) via an inversion–recovery pulse sequence technique under the deuterium lock mode.

Results and Discussion

Dielectric Relaxation Behavior. Figure 1 shows the ω dependencies of the real and imaginary parts of electric permittivity, ϵ' and ϵ'', for PVA-2000 in aqueous solution at $c_P = 1.49$ M and 25 °C as typical examples. According to the standard dielectric theory,[26] ϵ' and ϵ'' for the sample solutions are well decomposed into several sets of Debye-type relaxation functions as described by eq 1

$$\epsilon' - \epsilon_\infty = \sum_i \frac{\epsilon_i}{1 + (\omega\tau_i)^2}, \quad \epsilon'' = \sum_i \frac{\epsilon_i \omega^2 \tau_i}{1 + (\omega\tau_i)^2} \tag{1}$$

where ϵ_i and τ_i are the relaxation strength and time for a relaxation mode i, and ϵ_∞ is the high-frequency limiting value of electric permittivity. As summarized in Table 1, three relaxation components, i = w, 1, and 2, were necessary to precisely decompose the obtained spectra for all the examined PVA solutions.

A relaxation mode w, with the relaxation time, τ_w, and strength, ϵ_w, for a relaxation mode found at the highest frequency, was recognized as a rotational relaxation mode of water molecules with dynamics similar to that of pure liquid water (PW) molecules because the values of τ_w, and ϵ_w were close to those of $\tau_w{}^p$ and $\epsilon_w{}^p$ for PW as shown in Figure 2 containing c_P dependence of τ_w, and ϵ_w. It is well-known that the dielectric relaxation behavior of PW at 25 °C is perfectly described by eq 2 with the parameters $\tau_w{}^p = 8.3$ ps, $\epsilon_w{}^p = 73.1$, and $\epsilon_{\infty w}{}^p = 5.2$.[27]

$$\epsilon'_w{}^p - \epsilon_{\infty w}{}^p = \sum_i \frac{\epsilon_w{}^p}{1 + (\omega\tau_w{}^p)^2}, \quad \epsilon''_w{}^p = \sum_i \frac{\epsilon_w{}^p \omega \tau_w{}^p}{1 + (\omega\tau_w{}^p)^2} \tag{2}$$

Consequently, the fastest mode w was assigned to the rotational relaxation mode of free water molecules in the bulk aqueous phase. The additional relaxation modes of i = 1 and 2 were attributed to a mode that involves exchanging hydrated water (HW) molecules to PVAs and the micro-Brownian motions of PVAs at the monomer level with finite dipole moments (as

Table 1. Parameters Required To Decompose Dielectric Spectra for PVAs, CHDM, and CHDO in Aqueous Solution at 25 °C

$\bar{V}_m$/cm^3 mol^{-1}	c_P/M	$\Delta\epsilon_w$ (±0.1)	τ_w/ps (±0.02)	$\Delta\epsilon_1$ (±0.01)	τ_1 (±0.2)/ps	$\Delta\epsilon_2$	τ_2/ns	ϵ_∞ (±0.05)	Φ
				PVA-1000					
						(±0.01)	(±0.02)		
34.39	0.509	69.7	8.30	2.63	27.0	0.10	0.75	5.00	0.955
	0.714	68.3	8.25	3.90	27.0	0.14	0.70	5.00	0.936
	1.08	65.9	8.25	5.70	27.0	0.21	0.70	4.99	0.903
	1.49	63.3	8.25	8.60	28.0	0.33	1.00	4.24	0.867
	1.98	60.0	8.25	11.0	28.0	0.46	1.01	4.30	0.822
				PVA-2000					
						(±0.01)	(±0.02)		
33.18	0.499	69.8	8.30	3.00	29.0	0.10	0.75	4.70	0.956
	0.754	68.2	8.30	4.40	26.0	0.15	0.80	4.55	0.934
	0.993	66.7	8.30	5.25	27.5	0.23	0.90	4.50	0.913
	1.49	63.6	8.37	7.90	28.0	0.33	0.90	4.50	0.870
	2.06	60.1	8.45	10.5	28.0	0.43	1.00	4.40	0.821
				CHDM					
						(±0.1)	(±0.001)		
135.8	0.468	60.4	8.90	9.00	22.0			4.10	0.818
	0.681	55.0	8.90	12.5	22.0	1.1	0.035	4.27	0.745
	0.878	49.2	9.00	16.0	23.0	1.4	0.044	4.48	0.665
	1.24	40.0	9.00	22.5	23.0	2.0	0.075	3.50	0.541
	1.56	31.2	9.00	27.6	23.5	2.6	0.111	3.40	0.422
				CHDO					
						(±0.05)	(±0.001)		
103.5	0.473	62.0	9.00	8.69	19.1			5.22	0.838
	0.699	56.6	9.00	14.0	19.9	0.55	0.040	3.79	0.765
	0.908	51.5	9.00	18.0	22.0	0.70	0.050	3.78	0.696
	1.29	42.0	9.00	25.4	22.0	1.00	0.067	3.38	0.568
	1.73	32.0	9.00	33.5	23.7	1.40	0.090	2.97	0.433

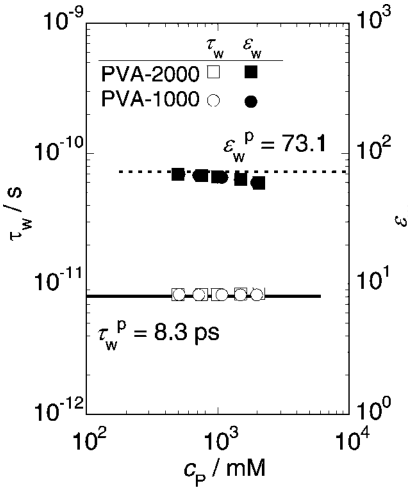

Figure 2. Dependence of τ_w and ϵ_w on c_P for aqueous PVA solutions.

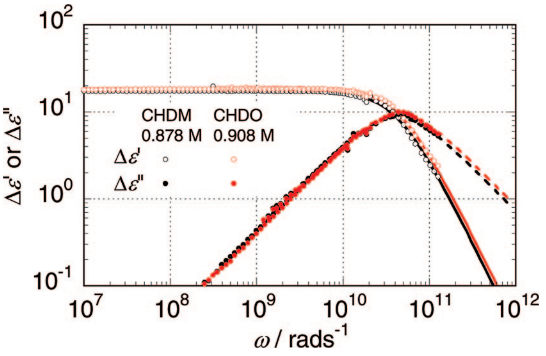

Figure 3. Differential dielectric spectra, $\Delta\epsilon'$ and $\Delta\epsilon''$ vs ω, for aqueous solutions of CHDM at $c = 0.878$ M and CHDO at $c = 0.908$ M. Solid and broken lines represent fitted spectra for the differential spectra calculated via eq 1 with parameters summarized in Table 1.

mentioned later). Figure 1 also contains the relaxation spectra of the bulk state water molecules in the solution, ϵ_w' and ϵ_w'' vs ω, and differential dielectric spectra, $\Delta\epsilon' = \epsilon' - \epsilon_\infty - \epsilon_w/(1 + \omega^2\tau_w^2)$ and $\Delta\epsilon'' = \epsilon'' - \epsilon_w\omega\tau_w/(1 + \omega^2\tau_w^2)$ vs ω, for the solution. A ratio of $\Phi = \epsilon_w/\epsilon_w^p$ indicates the fractional contribution of the whole water molecules in solutions to the w mode; i.e., at $\Phi = 1$, the sample is pure water. Solid and dotted lines representing ϵ', ϵ'', $\Delta\epsilon'$, and $\Delta\epsilon''$ were calculated using the parameters given in Table 1. Because agreement between the calculated lines and experimental data seems perfect, the reliability of the decomposition of ϵ' and ϵ'' with three Debye-type relaxation modes is reasonably high. Consequently, the differential dielectric spectra, $\Delta\epsilon'$ and $\Delta\epsilon''$ vs ω, were precisely determined for all the samples examined including low molar mass model alcohols. Table 1 also contains experimental uncertainties for each parameter determined to decompose ϵ' and ϵ'' data.

The differential spectra, evaluated by the same procedure as described above, for aqueous solutions of the model alcoholic substances possessing two OH groups without intramolecular hydrogen bonds, are shown in Figure 3. We can see that for CHDM at $c = 0.878$ M and 25 °C and CHDO at $c = 0.908$ M and 25 °C no distinctive difference was observed between the relationship of Φ and c for the two systems as tabulated in Table 1. The similarity displayed in Figure 3 is probably arises from the similar molecular structures. The differential spectra for CHDM and CHDO decomposed well into two relaxation modes irrespective of c as summarized in Table 1, the only exception being the data at the lowest c, which required only one component. These relaxation modes were attributed to the CHDM and CHDO molecules exchanging their attached HW molecules for bulk water molecules, and to the overall rotational motion of CHDM and CHDO molecules, in the same manner as was observed in aqueous PVA solutions.

Hydration Number and Structure. Since the concentrations of the sample solutions examined in this study were relatively low, hydrated PVA chains or CHDM molecules are sufficiently surrounded by bulk water molecules. Therefore, we can discuss the intrinsic hydration state and number, m, for a monomer unit of PVA (or the low molar mass alcohols) on the basis of the Φ data obtained. According to the previous studies, assuming rather separated relaxation modes of τ_w and τ_1 in aqueous solution, the value of Φ is directly related to the volume fraction of solute molecules, ϕ. In general, the electric permittivity, ϵ, of the solution consisting of a medium solvent (ϵ_m) and solute particle (ϵ_p) can be well described as a function of the solute particle volume fraction (ϕ) over a relatively wide range of ϕ as follows:[22,23,28]

$$\frac{\epsilon}{\epsilon_m} = \frac{(1 + \epsilon_p/2\epsilon_m)/(1 - \epsilon_p/\epsilon_m) - \phi}{(1 + \epsilon_p/2\epsilon_m)/(1 - \epsilon_p/\epsilon_m) + \phi/2} \qquad (3)$$

In the case of aqueous solutions without hydration effects, because ϵ_m ($= \epsilon_w^p$) = 73.1 (at 25 °C) and $\epsilon_p \sim 2-3$, eq 3 can be well approximated as $\Phi = \epsilon_w/\epsilon_w^p \sim (1 - \phi)/(1 + \phi/2)$.[29] It is well-known that this equation has been satisfied over a wide Φ range for simple aqueous systems consisting of many kinds of solute molecules without hydration effects, such as tetraalkylammonium bromide.[29] When a monomer unit of PVA (or a low molar mass alcohol) possesses tightly hydrated water molecules in aqueous solution, the relationship between Φ and c_P (or c) also includes important information related to the number of hydrated water molecules per monomer unit of PVA (or CHDM and CHDO molecules), m, as given by eq 4.[20–24,30–32]

$$\Phi = \frac{1 - 10^{-3}\bar{V}_m c_P}{1 + 10^{-3}\bar{V}_m c_P/2} - 10^{-3} m \bar{V}_w c_P \qquad (4)$$

Here, the partial molar volume of the solute, $\bar{V}_m$, and that of water, $\bar{V}_w$, should be expressed in units of cm^3 mol^{-1}. The hydrated water molecules no longer behave with solutes as bulk state water molecules with $\tau_w^p = 8.3$ ps, but their rotational molecular motion is detected as the relaxation mode $i = 1$ in aqueous solution. Because τ_w slightly depended on c_p and c, even at the same temperature as 25 °C, whether the ϵ_w^p value determined at 25 °C can be accepted for the evaluation of Φ is not clear. If ϵ_w^p is considered as a function of τ_w^p, the empirical relationship $\epsilon_w^p = 58.763 + 2.05\tau_w^p - 0.040(\tau_w^p)^2$ would provide ϵ_w^p by substituting τ_w instead of τ_w^p.[21,27] Although we employed this equation to evaluate Φ from ϵ_w here according to the previous study,[21] the greatest difference between Φ values calculated using the equation and the simple value of $\epsilon_w^p = 73.1$ was only 0.1 and 1.1% for aqueous solutions of PVAs and model compounds, respectively.

The dependence of Φ on c_P for aqueous solutions of PVAs with different n values is shown in Figure 4a,b. Lines in the figure represent the c_P dependence of Φ calculated via eq 4 with m values from 0 to 5. Since Φ data for both PVA-1000 (Figure 4a) and PVA-2000 (Figure 4b) lie on the line calculated at $m = 2$ (a line at $m = 2.2$ is most plausible for the data), it is concluded that monomer units of PVAs keep ca. 2−2.2 HW molecules in aqueous solution irrespective of n and c_P. Since the monomer unit of PVA possesses one OH group, m is identical to the average hydration number per OH group, m_{OH}, of PVAs in aqueous solution.

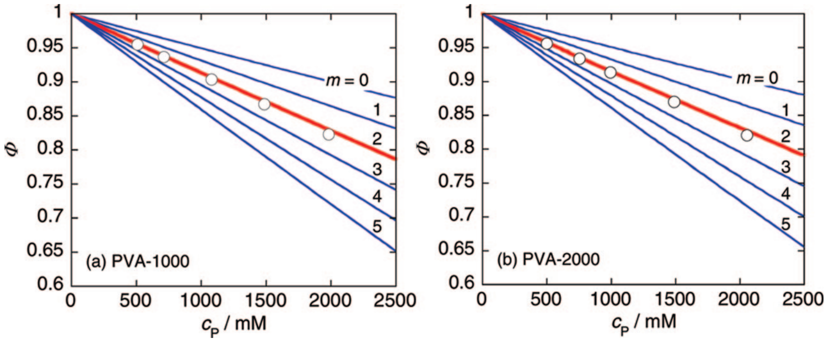

Figure 4. Relationship between Φ and c_P for aqueous solutions of PVA-1000 (a) and PVA-2000 (b). Lines represent the theoretical prediction via eq 4 with varying hydration numbers.

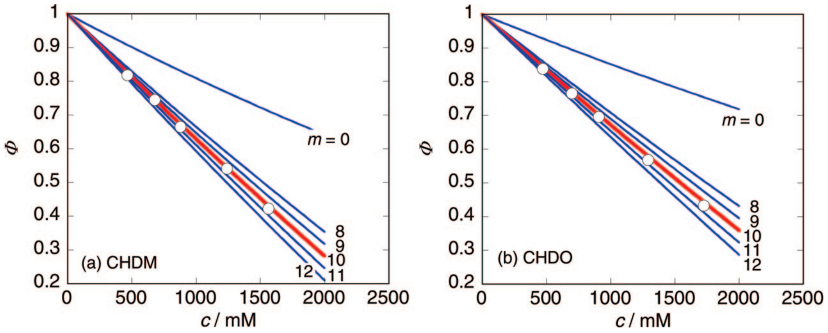

Figure 5. Relationship between Φ and c for aqueous solutions of CHDM (a) and CHDO (b). Lines represent the theoretical prediction via eq 4 with varying hydration numbers.

The value of $m_{OH} = 2$ is close to the number of water molecules in the first solvation shell, ca. 2.5, determined by integration of the partial radial distribution function of water oxygen atoms over the distance from PVA oxygen atoms calculated by molecular dynamics simulation for PVA with $n = 15$ in aqueous solution at 27 °C.[18] Tamai et al.[17] have also evaluated the coordination number of water molecules around an OH group to be ca. 2.2 using almost the same procedure. The slight difference between the hydration (coordination) numbers evaluated by the similar methods is attributed to a small difference in the upper boundary for the integration of partial radial distribution functions.[18]

Kaatze et al.[12] reported a value of ca. 5.1 for m for PVAs in aqueous solution based on precise dielectric data. The difference between their value of m and that obtained in this study is beyond the magnitude of experimental uncertainty. The analytical method employed in their study was not essentially different from methods used here. However, Kaatze et al. assumed that the relaxation strength of hydrated water molecules is identical to that of bulk water molecules without any basic evidence, whereas we did not make such an assumption. The differences in m values have also been reported for an aqueous poly(ethylene oxide) system.[24]

Conversely, the relationship between Φ and c for aqueous solutions of CHDM and CHDO is shown in Figure 5a,b. The value of $m = 10$ was evaluated irrespective of the solute species and c in the same procedure described above. Consequently, m_{OH} is calculated to be 5 by taking into account the fact that CHDM and CHDO molecules possess two OH groups in their molecular structures. It is worth noting that the hydration number of methanol was evaluated to be ca. 5 by ultrasonic velocity measurements.[33] Additionally, the hydration number of the free OH group is not influenced by whether the OH group belongs to primary (CHDM) or secondary (CHDO) OH groups.

The m_{OH} value is expected to be diminished by the hydrogen bond formation between OH groups. For example, dielectric relaxation measurements for aqueous solutions of cyclodextrins, which are water-soluble cyclic oligosaccharides possessing a number of OH groups, revealed that the intramolecular side-by-side hydrogen bond formation reduces m_{OH} to unity.[23] The order of $m_{OH}(\mathrm{PVA}) < m_{OH}(\mathrm{CHDM}) = m_{OH}(\mathrm{CHDO})$ strongly suggests the presence of the intramolecular hydrogen bond formation between adjacent OH groups of PVAs as schematically depicted in Figure 6. Through molecular dynamics simulation study, Müller-Plathe and van Gunsteren[18] have estimated the fraction of intramolecular hydrogen bonds between adjacent OH groups to be 0.95 in all intramolecular hydrogen bonds, including intermolecular bonds.

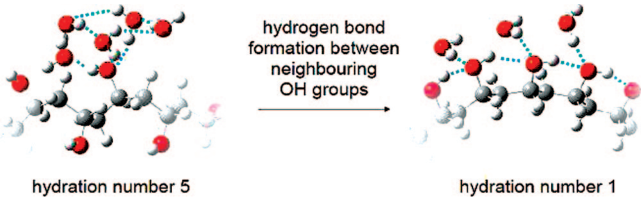

Figure 6. Schematic depiction of the effects of hydrogen bond formation between adjacent OH groups on the hydration number of OH groups of PVAs.

Here, we consider sequential hydrogen bond formation between adjacent OH groups of PVAs and assume the average number of OH groups in the sequential hydrogen bonding parts to be μ (cf. Figure 7). Then, the number of the hydrogen bonding sequences per PVA chain with the degree of polymerization, n, is given as $(n - f)/\mu$, where f is the number of free OH groups from the hydrogen bond formation. It is possible that the free OH groups, OH groups located at ends of the sequential hydrogen bonding parts, and OH groups forming the side-by-side hydrogen bonding in the sequential parts have distinct hydration states with different hydration numbers, as schematically depicted in Figure 7.

The hydration number of free OH groups is considered to be 5, similar to that of the OH groups of CHDM and CHDO that

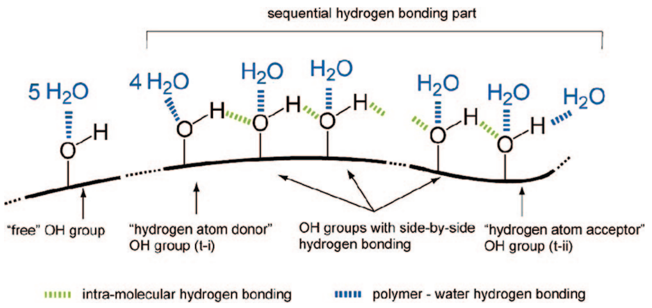

Figure 7. Schematic depiction of four types of PVA OH groups in aqueous solution, in relation to the formation of sequential hydrogen-bonding parts consisting of side-by-side hydrogen bonding.

are free from the hydrogen bonding. The OH groups forming the side-by-side hydrogen bonds seem to possess the hydration number of unity, taking into account the hydration number of cyclodextrins forming circular side-by-side hydrogen bonds.[23] In the case of OH groups at both terminal ends (t-i and t-ii) of the sequential hydrogen bonding parts, the hydration states are slightly complicated (cf. Figure 7). The oxygen atom of an OH group at a terminal end, t-i, of the sequential hydrogen bonding part, which supplies a hydrogen atom to an adjacent OH group to form a hydrogen bond, has a couple of lone pairs with the capacity for hydration. The hydration number of the OH groups is assumed to be 4, as observed in ether oxygen atoms of poly(ethylene oxide)s[24] and cyclodextrons.[23] On the other hand, the OH group at the opposite terminal, t-ii, after accepting a hydrogen atom from an adjacent OH group and supplying a couple of lone pair electrons, still possesses another couple of remaining lone pair electrons and a hydrogen atom that are free from the hydrogen bond formation between adjacent OH groups. Such an OH group should have the hydration number of 2 since both the remaining lone pair electrons and the free hydrogen atom behave as active hydration sites.

Consequently, the average hydration number per OH group, m_{OH}, is expressed by eq 5 with the parameters, μ and f.

$$m_{OH}=\frac{1}{n}\left\{\frac{n-f}{\mu}[1\times(\mu-2)+4+2]+5\times f\right\} \qquad (5)$$

When we substitute m_{OH} = 2 (and 2.2) and define the molar fraction of OH groups forming intramolecular hydrogen bonds as $x \equiv (n-f)/n$, the equation $\mu = 4x/(4x-3)$ (and $\mu = 4x/(4x-2.8)$ for $m_{OH} = 2.2$) is obtained. Because the value of μ must be greater than 2, x is evaluated to be $0.75 \le x \le 1$ (and $0.70 \le x \le 1$ for $m_{OH} = 2.2$). This value of x is larger than 0.4, which has been reported by molecular dynamic simulation studies.[17–19]

The formation of intramolecular hydrogen bonds between OH groups of PVAs in aqueous solution has been also proposed by single-molecule force spectroscopic studies using AFM[10] and NMR techniques.[11] In addition, the formation of six-membered rings[2] or multiple-stranded suprastructure[10] owing to intramolecular hydrogen bonding in aqueous PVA solutions have been proposed. Preferential hydrogen bond formation between adjacent OH groups suggested in this study is highly responsible to construct such the higher order structures.

Relaxation Times and Strengths. Each relaxation mode in the middle (i = 1) and slow (i = 2) frequency range is described well by one set of Debye-type relaxation functions. Parts a and b of Figure 8 show the c_P dependence of τ_i and ϵ_i (i = 1, 2) for aqueous solutions of PVAs, respectively. The value of τ_i barely depends on n and c_P, whereas ϵ_i is proportional to c_P. These observations imply that the two relaxation modes are relevant to the existence of solute PVAs.

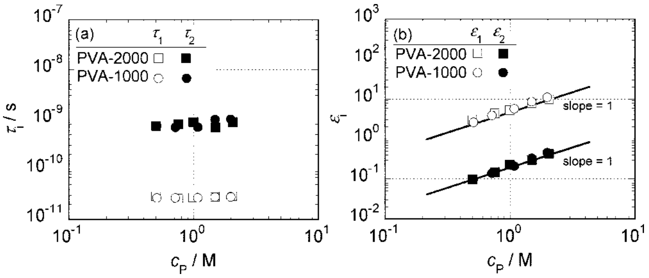

Figure 8. Dependence of τ_i (a) and ϵ_i (b) (i = 1, 2) on c_P for aqueous PVA solutions.

The relaxation mode of i = 1 has a relaxation time, τ_1, of ca. 28 ps irrespective of n and c_P. This τ_1 value is about 3 times as large as the rotational relaxation time of pure water molecules, $\tau_W{}^P$ (= 8.3 ps). Moreover, the relaxation mode with almost the same relaxation time is also observed for some other aqueous systems irrespective of their molecular size and structures.[20–24] These results strongly suggest that the relaxation mode i = 1 can be attributed to the reorientational relaxation mode of HW molecules relevant to the exchange of HW molecules associated with the hydrophilic moieties, OH groups of the solute molecules.

The dielectric relaxation strength of the relaxation mode i = 1 normalized with c_P and m, $\epsilon_1(c_P m)^{-1}$, was evaluated to be ca. 2.51 M^{-1}, which indicates the molar dielectric relaxation strength of the hydrated water molecules. This value is about twice as great as the molar dielectric relaxation strength of the bulk water molecules, ca. 1.32 M^{-1}, calculated from the dielectric relaxation strength of bulk water molecules, $\epsilon_W{}^P$ = 73.1, and the molar amount of bulk water, 55.6 M. Precise analysis for the relationship between the residence time for the exchanging process of HW molecules and their dielectric relaxation strength revealed that HW molecules that reside for longer times residence times at their hydration sites before the exchange process tend to exhibit stronger dielectric relaxation strengths.[23] These results also allow us to assign the relaxation mode i = 1 to the reorientation relaxation of HW molecules.

The relaxation time for the slow frequency mode of i = 2, τ_2, was evaluated as ca. 750 ps irrespective of n and c_P. For the assignment of the relaxation mode i = 2, we performed the ^{13}C NMR measurements to determine the correlation time, τ_c, of ^{13}C nuclei of PVA main chains. A ^{13}C nucleus covalently bonded to a ^{1}H nucleus always exhibits a magnetic dipole–dipole interaction, which relaxes the magnetization of the ^{13}C nucleus due to molecular motion agitating the magnetic field (with a time constant given as the correlation time, τ_c).[34]

In general, T_1 ^{13}C NMR determined under the complete proton decoupling condition is given by eq 6[35]

$$\frac{1}{NT_1}=\frac{\gamma_H{}^2\gamma_C{}^2h^2}{40\pi^2 r_{CH}{}^6}\left\{\frac{\tau_C}{1+9(\omega_r\tau_c)^2}+\frac{3\tau_C}{1+(\omega_r\tau_c)^2}+\frac{6\tau_C}{1+25(\omega_r\tau_c)^2}\right\} \qquad (6)$$

where N is the number of ^{1}H nuclei directly bound to ^{13}C, γ_H and γ_C are the magnetogyric ratios of ^{1}H and ^{13}C, respectively, h is Planck's constant, r_{CH} is the distance between ^{1}H and ^{13}C (1.09 Å), and τ_c is the correlation time of ^{13}C. Figure 9 shows the relationship between $(NT_1)^{-1}$ and ω_r for the methine and methylene carbons of PVA-2000 in D_2O. The obtained experimental data are described well by eq 6 with $\tau_c = 2.01 \times 10^{-10}$ s. The $(NT_1)^{-1}$ values calculated from the data reported by Petit and Zhu[35] for aqueous PVA solutions with $n \sim 1100$ are also plotted in Figure 9. Agreement between our and their data is perfect, as seen in this figure.

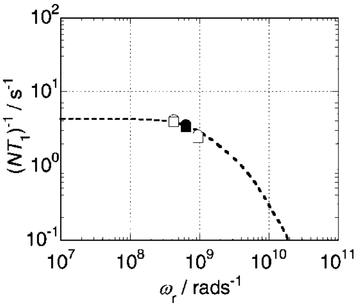

Figure 9. $(NT_1)^{-1}$ values for methine (open circle) and methylene (open square) ^{13}C nuclei of PVA-2000 in D_2O as a function of resonance frequency, ω_r. A broken line is calculated via eq 6 with $\tau_c = 2.01 \times 10^{-10}$ s. This figure also contains the $(NT_1)^{-1}$ values for the methine (filled circle) and methylene (filled square) ^{13}C nuclei reported by Petit and Zhu.[36]

The correlation time, τ_c, determined by T_1 ^{13}C NMR can be converted into a relaxation time with the same physical meaning as the dielectric relaxation time by multiplying by a factor of 3.[37] Thus, we can evaluate the (dielectric) relaxation time of the methine and methelene groups to be $\tau_d = 3\tau_c \sim 600$ ps. Because this τ_d value is close to the τ_2, motions of dipoles belonging to monomer units of PVAs are governed by molecular motions of adjacent methine and methelene groups. Consequently, the relaxation mode of $i = 2$ is assigned to the local motions of PVA main chains in aqueous solution, which should be relevant to either the lifetime of hydrogen bonds between adjacent OH groups in sequential hydrogen-bonding parts schematically depicted in Figure 7 or the rate of rotational motion of the sequential hydrogen-bonding parts with finite summed dipole moments of each constituent OH group. In the latter case, the lifetime of hydrogen bonds between adjacent OH groups is much longer than the rotational relaxation time of the sequential hydrogen-bonding parts assigned to the $i = 2$ mode.

Concluding Remarks

The hydration states and dynamics of poly(vinyl alcohol)s (PVAs) with different degrees of polymerization, and those of the low molar mass alcohols 1,4-cyclohexanedimethanol (CHDM) and 1,4-cyclohexanediol (CHDO) in aqueous solution, were investigated by using dielectric relaxation measurements at 25 °C over a wide frequency range up to 20 GHz.

The dielectric relaxation spectra of aqueous PVA solutions decomposed well into three sets of Debye-type relaxation functions assigned to the rotational relaxation of bulk state water molecules, of the exchange of hydrated water molecules to the OH groups of the PVA monomer units, and the local motion of the main chain of PVAs.

The smaller hydration number per OH group, ca. 2−2.2, was evaluated for PVAs in aqueous solution and compared to CHDM and CHDO, which displayed a hydration number of ca. 5. Taking into account the fact that the OH groups of these low molar mass alcohols do not form intramolecular hydrogen bonds, the smaller hydration number strongly suggests that the intramolecular hydrogen bonds are formed between OH groups of PVAs and that this reduces the hydration number to 2.

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