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The Interaction of Poly(ethylene glycol) with Water Studied by ^1H and ^2H NMR Relaxation Time Measurements

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ABSTRACT: In this paper NMR relaxation time investigations of water protons (^1H) and deuterons (^2H) in aqueous poly(ethylene glycol) (PEG) solutions are presented for the water content range of 3−90 wt %. The number of bound water molecules per PEG repeat unit is estimated to be one from the water relaxation times by using a model of fast exchange of water molecules between a bound and an unbound water fraction. For water contents lower than one water molecule per PEG monomer, large restrictions in polymer mobility occur which also influence water NMR relaxation. For these low water contents, small ranges of oriented PEG chains are present in the solutions resulting in observable quadrupole splittings in the ^2H NMR spectra.

I. Introduction

The water-soluble and nontoxic poly(ethylene glycol) (PEG) has a very simple chemical structure: $-(CH_2\text{-}CH_2O-)_n$. This polymer exhibits several remarkable properties, which have been reviewed by Harris.[1] The special properties of PEG in aqueous solution are used for many applications. Some of these are as follows: the purification of proteins on the basis of the formation of two-phase systems with other polymers (e.g. dextran),[2−4] the induction of cell fusion[5,6] and the movement of molecules across cell membranes,[1] and the adjustment of the water content of biological systems by using aqueous PEG solutions for the osmotic stress technique.[7−9] For these reasons, the interaction of PEG with water has been extensively studied. In these studies the structure of hydrated PEG molecules and the number N_b of bound water molecules per repeat unit are of special interest.

Valuable information about the water binding properties of aqueous PEG solutions can be obtained from various methods, including light scattering,[10,1] quasi-elastic neutron scattering,[12] viscosity measurements,[12] investigations of the solvency of water for salts,[13,14] calorimetry,[15−22] and nuclear magnetic resonance (NMR) measurements.[13,21,23,24] While some authors determined a water binding of 2−4 bound water molecules per repeat unit,[16−19] others report a value of $N_b = 1$.[12,20−22]

In this paper the interaction of PEG with water is investigated to obtain further information about the water binding of PEG which is defined by reduced mobility, anisotropic motion, and hydrogen bonding from water molecules to the polar oxygen atom of the PEG monomers. For these investigations NMR relaxation studies were chosen, because the mobility of water molecules can be directly observed by using ^1H and ^2H NMR experiments. ^2H NMR is especially useful for studying the rotation of water molecules in polymer solutions with ^2H_2O as solvent, because the NMR relaxation mechanism of deuterium is mainly intramolecular in origin in contrast to ^1H NMR relaxation which is also influenced by intermolecular contributions.

In a previous study, Hey *et al.*[21] interpreted the residual quadrupole splitting of ^2H_2O in partially crystalline PEG by the ability of water to “plasticize” PEG. Breen *et al.*[23] studied the dynamical behavior of water in aqueous PEG solutions by ^2H and ^{17}O NMR relaxation time measurements for water contents higher than 15 wt % and various molecular weights of PEG while Ling and Murphy[13] reported ^1H relaxation times for water contents higher than 25 wt %.

For the interpretation of the NMR relaxation behavior of water, various models have been developed.[14,25−30] Most of these models are based on fast exchange of water molecules between bound and unbound water compartments.[31] In this study the simplest of these models is used for the interpretation of the measured data—the fast exchange between an unbound and a bound water fraction. This fast exchange model is valid if the exchange of water molecules between the bound and the unbound fractions is fast with respect to the relaxation processes. Then the water NMR relaxation behavior is monoexponential, and the water relaxation rates, which are equal to the inverse relaxation times, are weighted averages of the intrinsic relaxation rates of the two fractions. If the relaxation times are investigated for varying water contents, it is possible to estimate the number and the rotational correlation times of the bound water molecules from this simple model. In order to determine the amount of bound water, it is necessary to remove all the unbound water from the solutions. Therefore, the measurements were extended to very low water contents (from 90 to 3 wt %). In addition to the relaxation time data, valuable information about water structure can be obtained from the NMR spectra themselves.

II. Theory

^{1}H NMR Relaxation. The NMR relaxation times strongly depend on the mobility of the molecules involved, especially on their rotational motion. For protons, the spin I of the nucleus is equal to $^1/_2$. If only intramolecular dipole−dipole interactions of the water molecules are present as a relaxation mechanism, the following equations are valid for the proton spin−lattice (T_1) and the proton spin−spin relaxation times (T_2) according to the Bloembergen−Purcell−Pound theory:[32,33]

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$$\frac{1}{T_1} = \frac{3}{10}\left(\frac{\mu_0}{4\pi}\right)^2 \frac{\gamma^4 \hbar^2}{r^6}\left(\frac{\tau_R}{1+\omega^2{\tau_R}^2} + \frac{4\tau_R}{1+4\omega^2{\tau_R}^2}\right) \quad (1)$$

$$\frac{1}{T_2} = \frac{3}{20}\left(\frac{\mu_0}{4\pi}\right)^2 \frac{\gamma^4 \hbar^2}{r^6}\left(3\tau_R + \frac{5\tau_R}{1+\omega^2{\tau_R}^2} + \frac{2\tau_R}{1+4\omega^2{\tau_R}^2}\right) \quad (2)$$

r is the distance between the protons in the water molecule, μ_0 is the magnetic field constant in vacuum ($4\pi \times 10^{-7}$ H m^{-1}), γ is the gyromagnetic ratio of protons (2.675×10^8 rad T^{-1} s^{-1}), $\nu = \omega/2\pi$ is the spectrometer frequency, and τ_R is the rotational correlation time of the water molecules. $\hbar$ is equal to $h/2\pi$ with Planck's constant $h = 6.626 \times 10^{-34}$ J s. For short correlation times ($\omega\tau_R \ll 1$), the following expression is valid:

$$\frac{1}{T_1} = \frac{1}{T_2} = \frac{3}{2}\left(\frac{\mu_0}{4\pi}\right)^2 \frac{\gamma^4 \hbar^2}{r^6}\tau_R \quad (3)$$

For higher correlation times, T_1 differs from T_2, and T_1 goes through a minimum. T_2 always decreases with increasing τ_R, until the so-called "solid limit" is reached. The temperature dependence shown in Figure 1 can be obtained by assuming an Arrhenius behavior for the motion:

$$\tau_R = {\tau_R}^0 \exp\left(\frac{E_A}{RT}\right) \quad (4)$$

with T the temperature, $R = 8.31$ J mol^{-1} K^{-1} the gas constant, E_A the activation energy, and ${\tau_R}^0$ the correlation time for $T \to \infty$.

^{2}H NMR Relaxation. Nuclei with a spin $I \geq 1$ possess an electrical quadrupole moment eQ which can interact with the electric field gradient eq. Fluctuations of the field gradient are the most important relaxation mechanism in the case of quadrupolar nuclei. For deuterium ($I = 1$) in ^2H_2O, the fluctuations of the magnetic field arise from the reorientation of the ^{2}H$-$O field gradient, i.e. from the rotation of water molecules. If only one correlation process with the time constant τ_q is present, the ^{2}H quadrupole relaxation times can be expressed by[34,35]

$$\frac{1}{T_1} = \frac{3}{10}\pi^2\chi^2\left(\frac{\tau_q}{1+\omega^2{\tau_q}^2} + \frac{4\tau_q}{1+4\omega^2{\tau_q}^2}\right) \quad (5)$$

$$\frac{1}{T_2} = \frac{3}{20}\pi^2\chi^2\left(3\tau_q + \frac{5\tau_q}{1+\omega^2{\tau_q}^2} + \frac{2\tau_q}{1+4\omega^2{\tau_q}^2}\right) \quad (6)$$

where $\chi = e^2qQ/h$ is the quadrupole coupling constant. Like the behavior of the ^{1}H spin$-$lattice relaxation times, T_1 goes through a minimum. The correlation time $\tau_{q,\min}$ in the minimum is given by

$$\omega\tau_{q,\min} \approx 0.616 \quad (7)$$

In the "extreme narrowing" region ($\omega\tau_q \ll 1$), T_1 is equal to T_2

$$\frac{1}{T_1} = \frac{1}{T_2} = \frac{3}{2}\pi^2\chi^2\tau_q \quad (8)$$

Inasmuch as the ^{2}H relaxation times in ^2H_2O are mainly intramolecular in origin, important information about the reorientation of water molecules and about water binding can be obtained from ^{2}H NMR relaxation behavior.

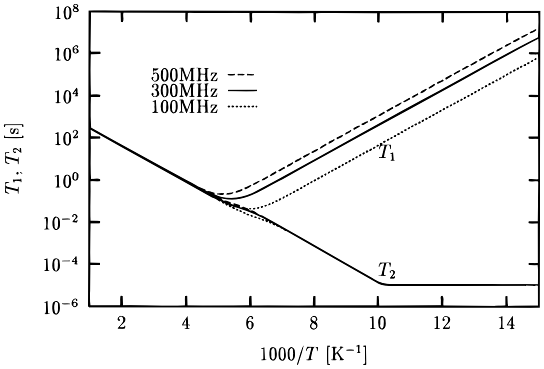

Figure 1. Theoretical temperature dependence of proton relaxation times T_1 and T_2 for intramolecular dipole$-$dipole interaction. T_1 and T_2 were calculated using eqs 1 and 2 with the parameters $\gamma = 2.675 \times 10^8$ rad T^{-1} s^{-1}, $r = 1.6$ Å, $E_A = 16$ kJ/mol and ${\tau_R}^0 = 5 \times 10^{-15}$ s for three different resonance frequencies ν: 100, 300, and 500 MHz.

Exchange Model. In the literature, the model of fast exchange between a bound and an unbound water fraction is often used to explain the NMR relaxation times T_l ($l = 1, 2$).[14,25–27,29,30] This model is based on the following equation:[31]

$$R_l = p_f R_{lf} + p_b R_{lb} \qquad l = 1, 2 \quad (9)$$

R_l is the observed mean relaxation rate defined by $R_l = 1/T_l$ and R_{lf} and R_{lb} are the intrinsic relaxation rates of the unbound and the bound water compartments, respectively. Experimentally, R_{lf}^{-1} is equal to 2 s for water protons and 450 ms for water deuterons from the study of bulk samples of ^1H_2O and ^2H_2O, p_f and p_b are the water fractions of the unbound and the bound compartments, respectively. With $p_f + p_b = 1$, eq 9 can be rewritten as

$$R_l = N_b(R_{lb} - R_{lf})N_M + R_{lf} \quad (10)$$

The constant N_b in eq 10 is equal to the number of bound water molecules per polymer repeat unit and N_M is the number of monomers per water molecule. Hence, R_l should be a linear function of N_M with slope $N_b(R_{lb} - R_{lf})$ if a single bound and an unbound water fraction are present. Assuming that N_b is constant for all water contents and that all unbound water is removed by reducing the water content of the solvated polymer, R_l should be equal to R_{lb} (Figure 2) and there will be no further variations in R_l. This discontinuity will occur when $N_M = 1/N_b$.

^{2}H NMR Spectra of ^2H_2O. The averaging of the quadrupolar interaction of ^{2}H nuclei which is present in liquid ^2H_2O is caused by the fast and isotropic rotation of the water molecules. As a result the ^{2}H NMR spectrum consists of an isotropic signal with a Lorentzian line shape. In the case of lipid dispersions or in oriented systems, the water molecules interacting with these systems show an anisotropic motion. This anisotropy prevents the complete averaging of the quadrupolar interaction and causes a splitting of the isotropic signal. This splitting is defined by the difference between the resonance frequencies of the main maxima and is called the quadrupole splitting $\Delta\nu_Q$. For systems which are not macroscopically oriented, the so-called "powder spectrum" is obtained. Introducing the order

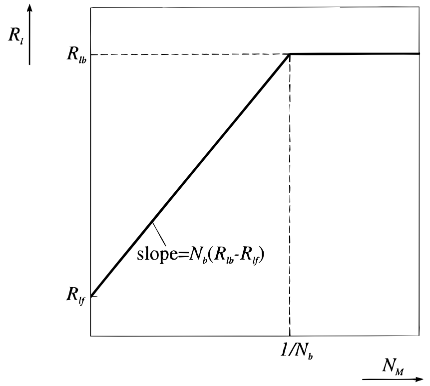

Figure 2. Water relaxation rate in the case of fast exchange of water molecules between an unbound and a bound water fraction as a function of the ratio N_M of the number of monomers to the number of water molecules.

parameter S which represents the degree of order and which is equal to the ratio of the measured to the maximum quadrupole splitting, the measured quadrupole splitting can be expressed by

$$\Delta\nu_Q = {}^3/_4\,\chi S \tag{11}$$

The value of S lies between 0 (complete averaging of the quadrupole interaction) and 1 (rigid ^2H_2O).

III. Materials and Methods

PEG with a mean molecular mass of 6000 was purchased from Serva. It was used without further purification, because intensive dialysis against deionized water did not change osmotic properties[36] or NMR relaxation times.[9]

Deionized ^1H_2O and ^2H_2O with an isotopic purity of 99.9% (Wilmad) were used as solvents for the aqueous PEG solutions. The solutions were not degassed. Measurements were conducted for water contents between 3 and 90 wt % in the PEG solutions.

For the NMR measurements, a Bruker AMX300 (^1H resonance frequency, 300 MHz) and a Bruker MSL100 (^1H resonance frequency, 100 MHz) were used. The NMR spectra were obtained by acquisition after a single $\pi/2$ pulse and subsequent Fourier transformation without filtering.

The spin−lattice relaxation times (T_1) were measured by using the inversion recovery sequence $\pi - t - \pi/2 - Acq$ with 15 different values for the time t. To determine the spin−spin relaxation times (T_2), the Carr−Purcell−Meiboom−Gill sequence $\pi/2 - (\tau - \pi - \tau)_n - Acq$ was used with an echo time τ of 200 μs and at least 15 different values for the echo number n. After Fourier transformation of the free induction decays, the intensities of the signals were obtained by integration. These intensities were used for the determination of T_1 and T_2. A multiexponential analysis of the relaxation data was performed by means of the least-squares curve-fitting software package Peakfit v.3 (Jandel Scientific).

IV. Results and Discussion

^{1}H and ^{2}H NMR Spectra. The ^1H NMR spectrum of an aqueous PEG solution shows two resonances separated by approximately 1.1 ppm. The signals at 4.8 and 3.7 ppm can be assigned to the water protons and the CH_2 protons of the PEG chains, respectively. Therefore, the relaxation times of both water protons and polymer protons can be measured. Figure 3 shows the ratio of the intensity of CH_2 protons (I_{CH_2}) to the intensity of water protons I_{H_2O} in the NMR spectra as a function of N_M. For $N_M < 1.5$ the intensity ratio I_{CH_2}/I_{H_2O} is a linear function of N_M with a slope of two. As expected, this slope is equal to the ratio of the number of monomer protons (four) to the number of water molecule protons (two). For $N_M > 1.5$, deviations from linearity in Figure 3 can be observed because of the invisibility of a part of the protons in the NMR spectra for low water contents resulting from the decreased polymer chain and water molecule mobilities. The apparent discontinuity in Figure 3 at about $N_M = 1 \ldots 1.5$ might be caused by errors in determining the integrals caused by overlapping of the signals, but can also result from structural changes in the solutions. Nevertheless, several flexible polymer chains exist even at very low water contents (3 wt %), because both signals in the ^1H NMR spectra can be observed for all investigated polymer concentrations.

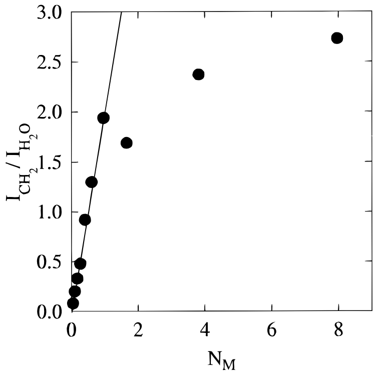

Figure 3. Ratio of the intensity of CH_2 protons (I_{CH_2}) to the intensity of water protons (I_{H_2O}) in the ^1H NMR spectra of PEG/water mixtures as a function of N_M (number of monomers per water molecule).

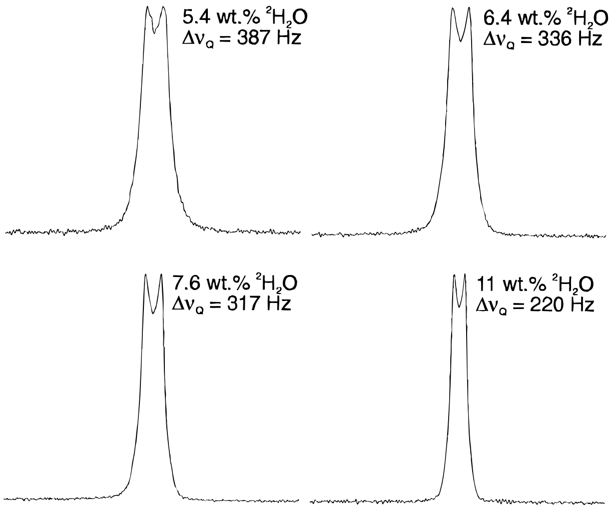

Figure 4. ^2H quadrupole splittings $\Delta\nu_Q$ of the water signal in PEG/^2H_2O mixtures for four concentrations and a resonance frequency of ν = 15.3 MHz.

For $N_M < 2.4$ (water content > 16 wt % ^2H_2O), the ^2H NMR spectra of PEG/^2H_2O mixtures consist of only one signal. For lower water contents, a splitting of this signal occurs (Figure 4). This splitting increases with decreasing water content and is in the range 150−500 Hz (Figure 5) at a temperature of T = 300 K. Inasmuch as the splitting does not depend on the resonance frequency (Figure 5), they can be assigned as quadrupole splittings. In the case of broad signals and small quadrupole splittings, the characteristic outer singularities of the spectra cannot be observed.[37,38]

The very surprising existence of quadrupole splittings is caused by an uncomplete motional averaging of water molecules within the relevant time range which is on the order of $1/\chi$. Quadrupole splittings can be observed in lipid bilayer suspensions[6,39−42] and also in oriented

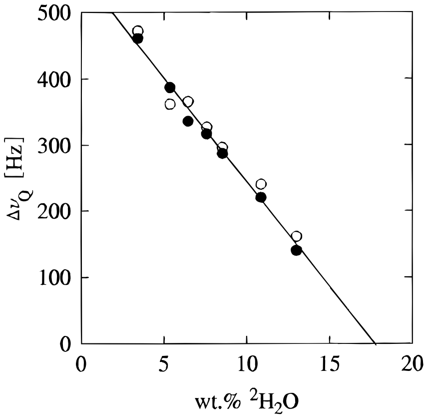

Figure 5. ^{2}H quadrupole splittings $\Delta\nu_Q$ of the water signal in PEG/^2H_2O solutions as a function of water content. The resonance frequencies 46 MHz (○) and 15.3 MHz (●) were used.

systems like oriented cellulose[43] and oriented collagen.[44] In contrast to PEG solutions, these systems are macroscopically oriented, whereas a macroscopic orientation of PEG/^2H_2O mixtures can be excluded in the present work.

Hey *et al.*[21] previously observed quadrupole splittings of PEG/^2H_2O solutions using PEG of higher molecular weight (8310 g/mol). The splittings are also approximately 500 Hz for water contents less than 5 wt % and were interpreted as resulting from fast but anisotropic motion of the water molecules. However, Hey *et al.* did not present an explanation for the origin of this anisotropy.

For the existence of the quadrupole splitting, it is necessary that the orientation of water molecules does not completely average in the time range of approximately $1/\chi$. The reason for that could be a strongly restricted motion of the water molecules. However, the relaxation times presented later in this paper are not very short, indicating a rather high mobility of the water molecules ($1/\chi \approx 6 \times 10^4 \tau_q$ for 11 wt % ^2H_2O). Hence, it is very likely that the water molecules responsible for the splitting exchange several times during the experiment. At least a portion of these exchanging water molecules cannot be randomly oriented, because otherwise the quadrupolar interaction would average to zero and no splitting could be observed. This is only possible if a part of the polymer chains is oriented. The presence of water is necessary for the formation of this structure, because water is able to pack the PEG chains[11] and form bridges between the oxygen atoms of the polymer.[45,46] Therefore, the crystalline structure shown in Figure 6a is expected to be partially present for water contents below 16 wt %. Dilute and semidilute PEG solutions show a weak anisotropic polymer dynamics while solutions of high PEG concentrations have additional internal polymer dynamics.[35] This change results in the structure shown in Figure 6a. The phase diagram given by Hager and MacRury[16] also shows the presence of crystalline structures for low water contents. For high water contents only one water molecule proton (deuteron) is bound to the PEG chains, whereas for $N_M > 1$ a part of water molecules is bound to the polymer by both protons (deuterons). In addition to the decrease in polymer mobility, this decrease in water molecule mobility is the reason the water relaxation times are not constant for $N_M > 1$. The order parameters S shown in Table 1 were estimated using eq 11 and are very small.

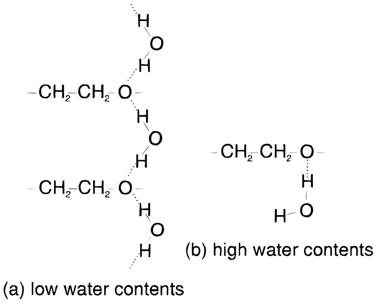

Figure 6. Structure of aqueous PEG solutions. For high water contents (b) a water molecule is bound to only one polymer chain, while for lower water contents (a) each of the two protons (or deuterons) of a part of water molecules is bound to a polymer chain, resulting in an orientation of water molecules.

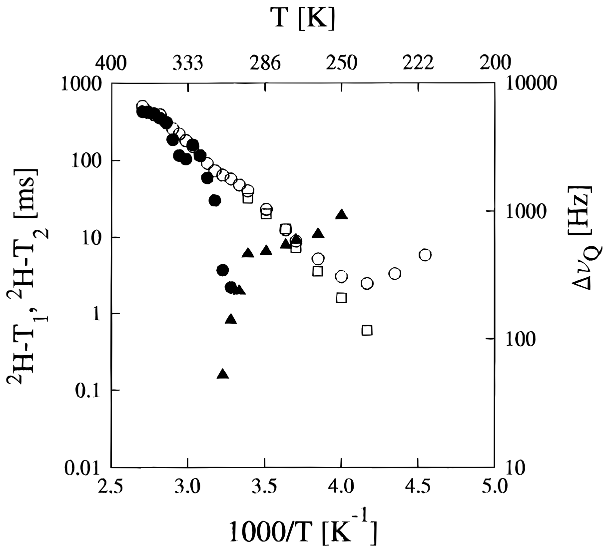

Figure 7. Temperature dependence of ^{2}H spin−lattice relaxation times ^2H-T_1 (○), ^{2}H spin−spin relaxation times ^2H-T_2 (●), and quadrupole splittings $\Delta\nu_Q$ (▲) of a PEG/^2H_2O mixture (water content 11 wt %). The values for ^2H-T_2 below 300 K (□) were measured immediately after cooling down from 370 K.

Table 1. Quadrupole Splittings $\Delta\nu_Q$ and Order Parameters S of PEG6000/^2H_2O Solutions for Two Different Resonance Frequencies Using Eq 11 and χ = 220 kHz

^2H_2O content (wt %)	N_M	ν = 15.3 MHz		ν = 46 MHz	
		$\Delta\nu_Q$ (Hz)	S	$\Delta\nu_Q$ (Hz)	S
3.4	12.91	461	0.0038	472	0.0039
5.4	7.96	387	0.0032	362	0.003
6.4	6.64	336	0.0027	366	0.003
7.6	5.53	317	0.0026	327	0.0027
8.5	4.89	287	0.0023	296	0.0024
11	3.68	220	0.0018	240	0.002
13	3.04	140	0.0011	161	0.0013

The temperature dependence of the quadrupole splitting was measured for a water content of 11 wt % (Figure 7). The splitting can only be observed for temperatures below 315 K. Above 315 K the splitting vanishes completely. This behavior can be explained by polymer chain "melting" and the loss of the order of the water molecules. This "melting" of crystalline structures at 315 K is in very good agreement with the phase diagram given by Hager and MacRury[16] in which "melting" is reported at approximately 318 K for 11 wt % water in solution with PEG of a mean molecular weight of 3510 g/mol. Cooling of the sample to 250 K

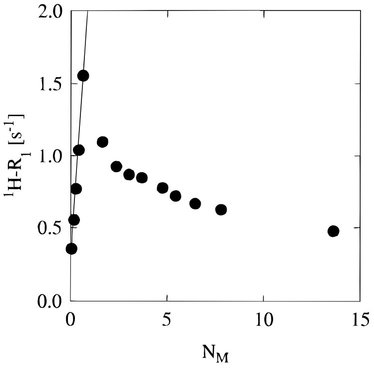

Figure 8. ^{1}H spin−lattice relaxation rates ^1H-R_1 of water protons of PEG/H_2O solutions as a function of N_M.

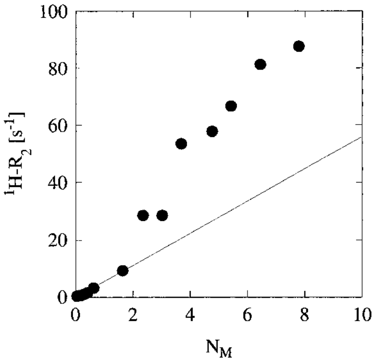

Figure 9. ^{1}H spin−spin relaxation rates ^1H-R_2 of water protons of PEG/H_2O solutions as a function of N_M.

was followed by a continuous increase of the splitting up to 1 kHz. Below 250 K no splitting can be measured because of the very broad signals corresponding to the short ^{2}H spin−spin relaxation times.

NMR Relaxation of Water Molecules and Polymer Segments. The spin−lattice and spin−spin relaxation rates of water protons ($1H$-R_1 and ^1H-R_2) are shown in Figures 8 and 9 as functions of N_M. For low N_M ^1H-R_1 is a linear function of N_M with a slope of 1.7 s^{-1} (Figure 8). This linear function can be explained by the fast exchange model. For $N_M > 1$ a completely different behavior is observed, the magnetization decay of the water signal becoming biexponential. The first component has very short ^{1}H spin−lattice relaxation times (2−10 ms) and is the minor component (<20% of the total intensity). The second component of water proton relaxation which is shown in Figure 8 has a much higher intensity and values for ^1H-R_1 of 1.7−0.5 s^{-1}. This relaxation rate decreases while N_M increases.

For $N_M < 1$ the spin−spin relaxation rate of the water protons (Figure 9) is also a linear function of N_M with the slope 5.6 s^{-1}. For $N_M > 1$ a biexponential relaxation can be observed. The component with the shorter relaxation time (2 ms) reflects the existence of solid-like regions in the PEG/water mixtures. In contrast to its spin−lattice relaxation rates, the spin−spin relaxation of the second component is faster than expected from the initial linearity. Therefore, the values of ^1H-R_2 are much higher than the values of ^1H-R_1 for $N_M >$ 1.

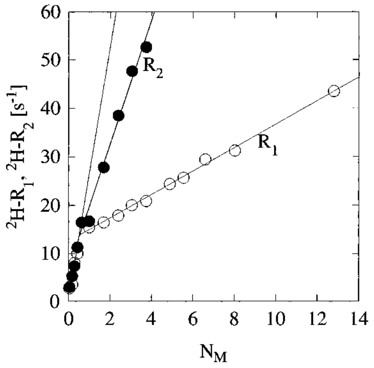

Figure 10. ^{2}H relaxation rates ^2H-R_1 (○) and ^2H-R_2 (●) of water deuterons of PEG/^2H_2O solutions as a function of N_M (number of monomers per water molecule).

Table 2. ^{2}H Spin−Spin Relaxation Times and Rotational Correlation Times τ_q of Water in PEG/^2H_2O Solutions

^2H_2O content (wt %)	N_M	^2H-T_2 (ms)	τ_q (ps)
90.7	0.05	337	3.7
71.9	0.18	191	4.8
62.2	0.28	136	10
51.8	0.42	89	15
42.2	0.68	61	22
31.6	0.98	60	23
21.2	1.69	36	38
16	2.39	26	53
13	3.04	21	64
11	3.68	19	75
8.5	4.89	1.4	1100
7.6	5.53	1.1	1500
6.4	6.65	1.0	1700
5.4	7.96	0.9	2000
3.4	12.91	0.5	6300

In contrast to the proton relaxation, the magnetization decay of water deuterons is monoexponential for all investigated PEG/^2H_2O mixtures. Figure 10 shows the spin−lattice (^2H-R_1) and spin−spin relaxation rates (^2H-R_2) of water deuterons as functions of N_M. For high water content ($N_M < 1$), ^2H-R_1 is equal to ^2H-R_2, and the relaxation rates are linear functions of N_M with a slope of 17 s^{-1}. For lower water content ^2H-R_2 is higher than ^2H-R_1. The values of ^2H-R_2 are very high for $N_M > 4$ and hence not shown in Figure 10 but listed in Table 2.

Assuming that the fast exchange model is valid, the linearity of all investigated NMR relaxation rates for $N_M \leq 1$ indicates that $N_b \leq 1$ must be valid according to eq 10. In other words, the PEG monomer does not bind more than one water molecule.

All measured water relaxation rates (^1H-R_1, ^1H-R_2, ^2H-R_1, ^2H-R_2) show deviations from the initial linearity for $N_M \geq 1$, indicating changes in water molecule dynamics. These changes are probably caused by the complete loss of unbound water at $N_M = 1$. Hence according to Figure 2, deviations from the linear increase of water relaxation rates can be observed and $R_l = R_{lb}$ is valid for $N_M = 1$. The slopes of all water relaxation rates for $N_M < 1$ are equal to $(R_{lb} - R_{lf})$. Therefore, both the slopes and the end of linearity at $N_M = 1$ indicate a binding of one water molecule per PEG monomer. The applicability of the fast exchange model is supported by the fact that the same amount of bound water can be determined from both the slope and the end of linearity.

This estimated value of one bound water molecule per monomer unit is in disagreement with values given by a number of investigators[16−19] but is also in good agreement with values determined by other investigators: The glass transition temperature has a minimum for $N_M = 1$,[20] and quasielastic light scattering and viscosity experiments indicate a binding of one water molecule per PEG monomer.[12] Calorimetry and melting

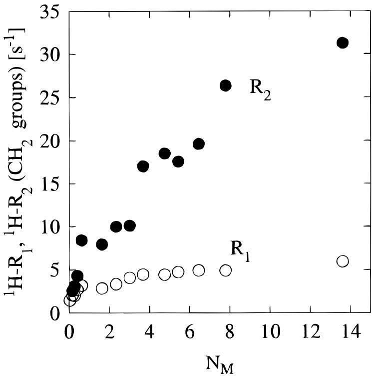

Figure 11. ^{1}H relaxation rates ^1H-R_1 (○) and ^1H-R_2 (●) of CH_2 protons of PEG/H_2O solutions as functions of N_M.

point investigations also indicate a binding of one water molecule.[21,22]

The increase of proton R_1 and R_2 of the polymer CH_2 groups with increasing N_M and the differences between R_1 and R_2 (Figure 11) are caused by reduced polymer chain mobility at low water contents. The decreased polymer motion is accompanied by a corresponding loss in the mobility of the bound water molecules. This means that for low water contents R_{lb} cannot be a constant value but depends on water content. This is the reason for the considerable deviations of water relaxation rates from the ideal behavior shown in Figure 2 for $N_M > 1$.

Equations 1, 2, 5, and 6 indicate that very slow reorientations result in very long intrinsic spin−lattice and very short intrinsic spin−spin relaxation times. Hence according to eq 9, very slow processes do not contribute to spin−lattice relaxation; the observed spin−spin relaxation times, however, are strongly reduced by slow motional processes. Therefore, the differences between T_1 and T_2 for both proton and deuterium relaxation of water molecules for $N_M > 1$ are also caused by the slow reorientation of water molecules.

Because of the large influence of slow processes on water relaxation after the removal of unbound water, it is possible that the water proton T_1 values are on the right-hand side of its minimum value in Figure 1 and increase with decreasing water content.

Deuterium T_1 and T_2 values of a PEG/^2H_2O mixture containing 11 wt % water are shown in Figure 7. Assuming an Arrhenius behavior for τ_q comparable to eq 4, the logarithmic relaxation times are linear functions of the inverse absolute temperature in the temperature range between 370 and 330 K according to eq 8. In this range the deuterium T_1 and T_2 values are equal. The activation energy of 34 kJ/mol represents an energy between one and two hydrogen bonds. This value is consistent with an exchange process involving the structure shown in Figure 6. The hydrogen bonding between water molecules can be neglected, because no unbound water exists for this water content.

For temperatures below 330 K the deuterium T_2 value is considerably smaller than T_1: ^2H-T_1 has a minimum at 240 K, and ^2H-T_2 rapidly decreases below 1 ms and cannot be measured. The differences between ^2H-T_1 and ^2H-T_2 in this temperature range arise from the hindered rotation of a portion of the water molecules. These water molecules do not contribute to ^{2}H spin−lattice relaxation but only to ^{2}H spin−spin relaxation. Besides the very slow reorientational processes which do not contribute to the ^2H-T_1 value, ranges of considerably shorter correlation times must occur which determine ^2H-T_1. By heating the sample above 330 K the very slow reorientation of water molecules vanishes. Hence, ^2H-T_1 is equal to ^2H-T_2 for temperatures above 330 K.

If the sample is cooled from 370 to 300 K, the rigid polymer structures present before heating cannot be formed immediately, resulting in the equality of ^2H-T_1 and ^2H-T_2 even for low temperatures (Figure 7). To form the rigid polymer structures again, a storage of the sample at room temperature for a period of approximately 3−6 days is necessary.

Using eq 7 and $\nu = 46$ MHz, the correlation time $\tau_{q,min}$ at the minimum of ^2H-T_1 can be determined to be $\tau_{q,min} = 2.13$ ns. By means of this value, $T_{1,min} = 2.4$ ms, and using eq 5 the quadrupole coupling constant χ can be estimated to be $\chi \approx 172$ kHz. This value is slightly smaller than the value of $\chi \approx 220$ kHz given in literature.[6,39]

With $\chi = 220$ kHz the rotational correlation times τ_q of the reorientations of the water molecules can be determined. For $N_M \leq 1$, ^2H-T_1 is equal to ^2H-T_2. Hence, eq 8 can be used to determine τ_q. For $N_M = 0$, the well-known value for pure water of $\tau_q = 3$ ps can be determined. This rotational correlation time shows a linear increase with rising N_M and reaches a value of 23 ps for $N_M = 1$. This increase of the rotational correlation time is a result of the decrease of the fraction of unbound water and hence of the increasing influence of bound water. Inasmuch as all water molecules are bound for $N_M = 1$, the correlation time for the rotation of bound water molecules is equal to 23 ps. For higher values of N_M the correlation time of bound water molecules becomes dependent on polymer concentration. For $N_M > 1$, eq 6 must be used to determine the rotational correlation times. Table 2 shows that the values for the correlational motion of bound water molecules increases to approximately 6 ns for increasing N_M up to 12.8.

V. Conclusions

The facts that the water NMR relaxation is monoexponential and that water NMR relaxation rates are linear functions of N_M for $N_M < 1$ support the assumption that the fast exchange model is valid in this range of water content. Consequently, the number of bound water molecules cannot be larger than one. This is in agreement with the structure suggested by Molyneux[45] which is shown in Figure 6. According to this structure model, for high water contents one water molecule is bound per PEG monomer. The PEG/water structure considerably changes for low water contents. For $N_M > 1$, a strong motional restriction of polymer chains is present followed by a reduced mobility of bound water molecules and hence in a changed relaxation behavior. Some water molecules then form bridges between two microscopically ordered PEG chains, i.e. these water molecules have two hydrogen bonds with the oxygens of different polymer chains. As a consequence these water molecules show a strong anisotropic motion resulting in the observed quadrupole splitting of the ^{2}H NMR signal. Therefore, ranges of ordered and unordered water molecules exist for low water contents resulting in the observed multiexponential NMR relaxation.

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