

NMR Relaxometry Study of the Interaction of Water with a Nafion Membrane under Acid, Sodium, and Potassium Forms. Evidence of Two Types of Bound Water

Feina Xu,^{*,†,‡} Sébastien Leclerc,^{†,‡} and Daniel Canet^{§,⊥}

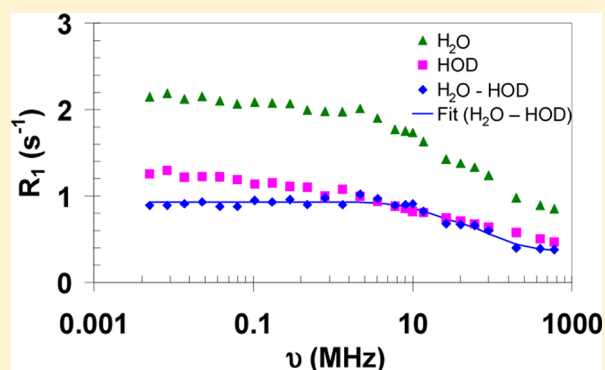
[†]Université de Lorraine, LEMTA, UMR 7563, Vandœuvre-lès-Nancy, F-54500 France

[‡]CNRS, LEMTA, UMR 7563, Vandœuvre-lès-Nancy F-54500, France

[§]Université de Lorraine, CRM2, UMR 7036, Vandœuvre-lès-Nancy F-54500, France

[⊥]CNRS, CRM2, UMR 7036, Vandœuvre-lès-Nancy F-54500, France

ABSTRACT: Through ^1H NMR relaxometry techniques (determination of the spin–lattice relaxation time as a function of the NMR measurement frequency), we have investigated, on a molecular scale, the water behavior in Nafion NRE 212 under acid, sodium, and potassium forms, the latter arising from different chemical treatments (with and without EDTA). Quantitatively, it turns out that (i) EDTA removes unwanted cations that may affect water mobility and (ii) the natural counteranions (sodium and potassium) also affect water mobility according to their size. In order to go further, we have developed a new methodology that rests on the comparison between samples prepared with H_2O and D_2O . For the latter, residual protons allow us to exclusively access intermolecular contribution to proton relaxation and, thus, enable us to deduce the intramolecular contribution of proton relaxation in H_2O . The analysis of this contribution reveals, for the first time, two types of bound water in Nafion.



1. INTRODUCTION

Owing to their particular mechanical, thermal, and (electro-)chemical properties, perfluorosulfonated membranes such as Nafion are widely used in separation processes, in particular, in proton exchange membrane fuel cells (PEMFCs).^{1–4} Although Nafion exhibits a high protonic conductivity when hydrated, this feature depends mostly on its water content. As a consequence, good water management is needed to ensure good performance in a running fuel cell. Indeed, a flooding of electrodes or a dehydration of membranes can lead to a decrease of fuel cell performance. In order to achieve optimum water management, it is desirable to characterize the mechanisms of water transport in all components of PEMFC, notably in Nafion membrane.

Although Nafion is the most popular and studied polymer electrolyte, results from the literature have to be taken with caution due to the membrane history. It is well-known that thermal and chemical treatments on the one hand and conditioning on the other hand affect the swelling of the membrane and, consequently, its performance.^{5,6} Eventually, for modeling purpose, we have to apprehend the water behavior in Nafion for a given chemical treatment or membrane history. As the structure of Nafion^{7–9} varies with its water amount, it should be interesting to probe Nafion on different scales. The aim is to relate the water behavior in Nafion to a

given membrane history on different scales and through a wide range of water content.

Among all nonintrusive techniques, ^1H NMR is a suitable tool for exclusively detecting water because Nafion possesses a perfluorosulfonated backbone. One can use ^1H NMR for measuring water dynamics on a microscopic scale by space labeling with magnetic field gradients^{10,11} and on a molecular scale by an appropriate interpretation of nuclear spin relaxation times.^{12,13} Concerning the latter, they may be affected by the presence of paramagnetic cations inside of samples that may complicate their interpretation. Thus, some caution has to be exercised before studying Nafion by ^1H NMR. For this purpose, the use of EDTA (ethylenediaminetetraacetic acid) is suggested in the literature.^{14–16} Although it is well-known that EDTA is capable of removing paramagnetic cations by complexation, its use in the case of Nafion provokes an exchange of counteranions because this acid is not soluble in water, contrary to the salted forms (sodium, potassium, etc.).

In previous work,¹⁷ we studied the impact of counteranions on the water diffusion in Nafion treated with or without EDTA salts (sodium and potassium forms). We observed that protons within Nafion in its acid form diffuse more rapidly than those in

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sodium or potassium forms. This feature can be easily explained by the lability of oxonium ions within Nafion in its acid form; they can be transported by proton hopping via two mechanisms, vehicle and Gröthaus. In addition, we also showed that the use of EDTA has no influence as far as translational diffusion measurements are concerned; the water diffusion in Nafion in its acid form was the same with or without the use of EDTA salts. However, this behavior could be very different on a smaller scale because the interaction between the water proton and their environment should normally be stronger. Consequently, it appears interesting to turn to spin relaxation and more precisely to NMR relaxometry.

NMR relaxometry consists of determining the longitudinal or spin–lattice relaxation time (T_1) of the water protons over a wide range of Larmor frequencies (ν , the frequency at which the NMR measurement is performed). Measurements of T_1 over a large frequency range could be time-consuming and tedious. Such measurements are alleviated by the use of fast field cycling (FFC) spectrometers, which generally span 3 decades in the low-frequency range, starting from 5 kHz. In this way, NMR relaxometry has become the method of choice for investigating the dynamics of organized systems such as polymers, solid electrolytes, biomolecules, and liquid crystals.^{18–20} In fact, this technique is useful whenever slow motions or interaction with paramagnetic species render the relaxation time dependent on the Larmor frequency. In that case, experimental results are presented in the form of the so-called dispersion curves, which are a plot of the relaxation rate R_1 ($R_1 = 1/T_1$) as a function of the Larmor frequency. Besides the presence of slow motions and/or paramagnetic species, the analysis of dispersion curves can lead to quantities called correlation times (generally denoted by τ_c), which characterize the different rotational motions experienced by the molecule of interest (τ_c can be viewed as the time necessary for the molecule to reorient by 1 rad).

NMR relaxometry has already been applied to the study of water dynamics in Nafion membranes,^{15,16,21} demonstrating thereby the interest of the technique. Although the measurement of T_1 over a wide range of Larmor frequencies is relatively easy, it turns out that the interpretation of results remains rather difficult. In fact, each new system needs an appropriate model for both understanding the shape of the dispersion curve and possibly extracting meaningful correlation times. This latter point is important for explaining the interactions between water molecules and their environment. For instance, we could not find in the literature any value of τ_c for Nafion in the acid form. In contrast, some τ_c values related to Nafion impregnated with various cationic ionic liquids were recently proposed;¹⁹ correlation time values ranging from 0.8 to 1.18 ns were determined for Nafion samples impregnated with three different cationic ionic liquids and at very different water contents.

Here, we propose to compare proton dispersion curves of water within Nafion under various cationic forms, such as H^+ , Na^+ , and K^+ , arising from four different chemical cleaning methods with or without soaking in an EDTA solution. In order to go further in the interpretation, we have considered two mechanisms of relaxation, intra- and intermolecular. The intermolecular contribution was obtained from the proton dispersion curves of HOD (residual proton from deuterated molecules). This contribution is subtracted from the proton dispersion curves of H_2O in order to access the intramolecular contribution. Indeed, the interpretation of the latter stems only

from the intramolecular H–H dipolar interaction, making it possible to determine a meaningful correlation time associated with each type of motion or each type of water. Moreover, thanks to dedicated instruments, we were able to investigate a very large Larmor frequency range (5 kHz–600 MHz) and thus to derive more reliable parameters. As membrane history is important to understand the results, we have described in more details the preparation of samples in the following section.

2. EXPERIMENTAL SECTION

2.1. Materials. Nafion NRE-212, a nonreinforced dispersion-cast membrane, was purchased from Ion Power Inc. and used throughout this work. All salts listed below were purchased with purities higher than 99% from Sigma-Aldrich and were used without further purification: LiCl, KCH_3COO , $MgCl_2$, K_2CO_3 , $Mg(NO_3)_2 \cdot 6H_2O$, NaCl, KCl, $BaCl_2$, $KClO_3$, EDTA disodium salt dehydrate ($C_{10}H_{14}Na_2N_2O_8$ or EDTA- Na_2), and EDTA dipotassium salt dehydrate ($C_{10}H_{14}K_2N_2O_8$ or EDTA- K_2). D_2O with a 99.90% enrichment was purchased from EURISO-TOP. Acids with the quality upgraded, such as HCl (37 wt %), H_2SO_4 (95–97 wt %), and HNO_3 (65% wt), were purchased from Sigma-Aldrich and used as received. Pure water produced by a reverse-osmosis apparatus from Onda (Purite 1 Select) was used for preparing solutions and washing NMR tubes.

2.2. Sample Preparation. NMR tubes (10 mm o.d. from Wilmad-Labglass) were cleaned using a protocol similar to the one described by MacMillan¹⁴ in order to remove possible metallic cations; all tubes were immersed in a mixture of acid solutions (50% of H_2SO_4 + 50% of HNO_3 , 1 mol L^{-1}) for 24 h. They were then rinsed at least four times with distilled water before being immersed in an ultrasound bath in order to remove any trace of impurities. They were subsequently soaked in a solution of EDTA- Na_2 (0.015 mol L^{-1}) for at least 24 h. Thereafter, all tubes were rinsed thoroughly with distilled water before being immersed again in an ultrasound bath. Finally, they were rinsed again and dried in an oven at 60 °C overnight.

The pristine membrane Nafion NRE-212, with an equivalent weight of 1100 g equiv⁻¹ and a mean thickness of 50 μm , was cut into pieces of 1.1×30.5 cm. All strips were boiled in H_2O_2 (3 wt %) for 1 h in order to remove organic impurities that could come from Nafion manufacturing. They were then rinsed in pure water at room temperature before being boiled in pure water for 1 h. After that, all strips were separated into two groups to be prepared either with H_2O or with D_2O .

Samples Prepared with H_2O : (1) *Samples in acid form:* H^+ . The strips of Nafion were prepared in acid form by soaking in a 2 mol L^{-1} of HCl solution for 2 h at 80 °C. They were then rinsed several times with pure water at room temperature prior to immersing them in demineralized water for 2 h at 80 °C. Subsequently, they were acidified again in a 1 mol L^{-1} of HNO_3 solution for 2 h at 80 °C. All samples were afterward rinsed thoroughly in pure water at room temperature, and all excess of acid within the samples was removed by cleaning twice in distilled water at 80 °C for 2 h.

(2) *Samples in sodium form:* Na^+ . The samples Na^+ were obtained by following a similar setup as that described by MacMillan.¹⁴ The samples were first acidified according to the samples H^+ . Then, they were soaked in a solution of EDTA- Na_2 at 0.015 mol L^{-1} for more than 3 days; the soaked solution was changed at least five times. Thereafter, they were thoroughly rinsed with pure water before being cleaned twice in demineralized water at 80 °C for 2 h.

(3) *Samples in acid form and treated with EDTA:* $H^+-Na^+-H^+$. First, the samples were prepared according to (2). Second, they were acidified with a solution of HNO_3 at 1 mol L^{-1} at 80°C for 2 h. Finally, they were rinsed twice in pure water at 80°C for 2 h.

(4) *Samples in potassium form:* K^+ . The setup was the same as that described above for the Na^+ samples. However, we used $EDTA-K_2$ in place of $EDTA-Na_2$ salt.

Once the samples (1–4) were prepared, they were dried in an oven at 60°C overnight before being introduced by pair in rolled form at the bottom of each NMR tube. In order to avoid the effects of a possible hydration of the rolled membranes into each NMR tube during the insertion step, they were dried again at 60°C overnight prior to equilibration in a given relative humidity. Thereafter, the dry mass of each pair of rolled membranes within the NMR tube was weighted; the typical weight for two strips was around 0.7 g. Samples were subsequently hydrated at room temperature in a sealed jar for at least 3 months, with water vapor generated by hygroscopic salt solutions. In order to cover a large range of water relative humidities, -11.3 , 22.5 , 32.8 , 43.2 , 52.9 , 75.3 , 84.2 , 90 , and 98% at 25°C , we had to use the following salts, respectively: $LiCl$, KCH_3COO , $MgCl_2$, K_2CO_3 , $Mg(NO_3)_2 \cdot 6H_2O$, $NaCl$, KCl , $BaCl_2$, and $KClO_3$. The water content (expressed by λ) of the four series of samples (prepared in H_2O) for the above range of relative humidities is displayed in Figure 1. λ is calculated

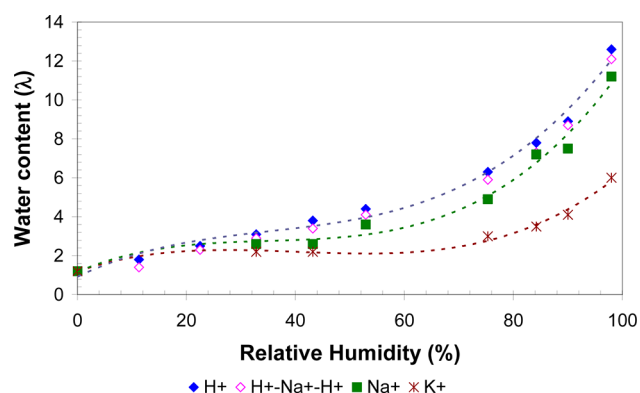


Figure 1. Water content of Nafion NRE 212 expressed by λ after 3 months of hydration.

according to eq 1.²² As the dry mass depends mostly on the experimenters and setup conditions, the remaining nonfree water (λ_0) has to be included in the equation giving λ . According to our previous work,¹⁷ $\lambda_0 = 1.2$.

$$\lambda = \frac{EW^+}{M_{H_2O}} \times \frac{m_{H_2O}}{m(\text{dry})} + \lambda_0 \quad (1)$$

where EW^+ is the equivalent weight of Nafion ($EW = 1100 \text{ g} \cdot \text{mol}^{-1}$) corrected for the exchanged cation C^+ and expressed by the forthcoming eq 2. Here, $M_{H_2O} = 18 \text{ g} \cdot \text{mol}^{-1}$, $m_{H_2O} = m(\text{wet sample}) - m(\text{dry})$, and $m(\text{dry}) = \text{mass of sample obtained at } 60^\circ\text{C}$.

$$EW^+ = EW + (M_{C^+} - 1) \quad (2)$$

Here, M_{C^+} is the molar mass of the cation.

Samples Prepared with D_2O . Samples were first prepared according to methods (1–4). They were then dried for 30 min in an oven at 60°C prior to being immersed in pure D_2O

(99.90% D) for at least 48 h. They were afterward dried again in an oven at 60°C overnight before being inserted by pair in rolled form into NMR tubes. The dried mass of the samples was determined after a last drying step in an oven at 60°C overnight. In order to reach a water content (expressed in λ) similar to that of the samples prepared with H_2O and to avoid direct contact of the material with heavy water, we first laid the NMR tube containing the membrane at its bottom, and we introduced at the opposite end the appropriate amount of D_2O . The NMR tube was then sealed. As the deuterated water was very gradually vaporized in the NMR tube and absorbed by the rolled Nafion samples, 2 months were necessary to prepare the samples. Note that the water content in deuterated form, expressed in λ , was calculated according to eq 1 with $M_{D_2O} = 20 \text{ g} \cdot \text{mol}^{-1}$, even though a part of D_2O can be converted into HOD during the conditioning period.

2.3. NMR Experiments. The longitudinal (spin–lattice) relaxation time T_1 was measured at ambient temperature (296 K) with several instruments to cover the largest available frequency range. From 5 kHz to 10 MHz, a Stellar Smartracer relaxometer was used according to FFC procedures. At 200, 400, and 600 MHz, T_1 was measured according to the inversion–recovery sequence with standard vertical magnet NMR spectrometers. Instruments able to perform measurements in the 40 MHz (highest frequency of commercial relaxometers) to 100 MHz range are not easily available. In fact, as will be seen later, the 10–100 MHz frequency range is essential for our samples. The availability of a variable-field electromagnet with a homemade console allowed us to carry out T_1 measurements (still according to the inversion–recovery sequence) from 8 up to 90 MHz, thus with an overlap with the relaxometer results and a check of the consistency of the whole set of data.

3. RESULTS AND DISCUSSION

3.1. A First Overview from the 5 kHz–10 MHz Data. At the onset, we examine the relaxometer data for H_2O samples from the four protonated series under acid, sodium, and potassium forms. The corresponding dispersion curves are shown in Figure 2. From the latter, it can be pointed out that the relaxation rate of water in Nafion depends considerably on (i) the cleaning procedure, (ii) the type of counteranion in the polymer electrolyte, and (iii) the water amount. Point (i) can be evidenced by comparing both series in acid form treated with and without EDTA, H^+ , and $H^+-Na^+-H^+$, in particular, at low water contents; $R_1(H^+)$ is 10 times higher than $R_1(H^+-Na^+-H^+)$ at λ around 1.4–1.6 and at the lowest Larmor frequency (5 kHz). This result can be explained by the presence of paramagnetic impurities, such as divalent cations, in the H^+ samples. We can envision two consequences of these paramagnetic species: (i) water relaxation is enhanced by the interaction with the spin of the unpaired electron, and (ii) hydration of these divalent cations may slow down water reorientation. Thus, the use of EDTA is recommended for getting rid of these unwanted cations.

Concerning point (ii), it seems that the size of the counteranions affects the relaxation rate at a given water content. For instance, the relaxation rate R_1 is 5.7, 13.2, and $27.4 \text{ (s}^{-1}\text{)}$ for the samples treated with EDTA in acid, sodium, and potassium forms, respectively, measured at a Larmor frequency of 5 kHz and for λ values around 4–5. However, this effect is seen to become negligible when the water content

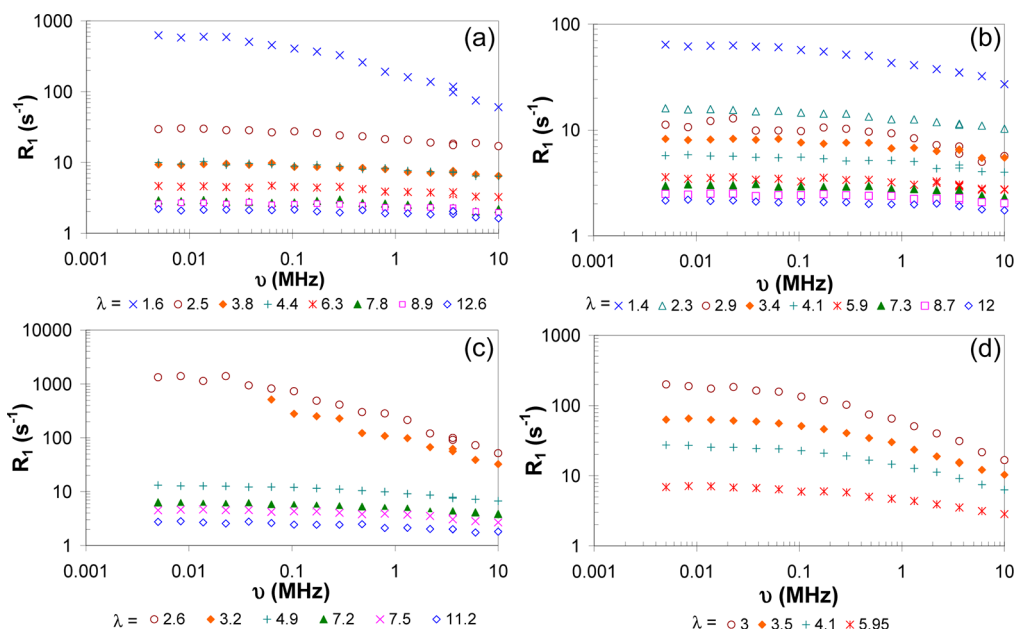


Figure 2. The 5 kHz–10 MHz dispersion curves of water protons in Nafion under different forms and at different hydration levels (λ) obtained by FFC relaxometry: (a) H^+ , (b) $\text{H}^+-\text{Na}^+-\text{H}^+$, (c) Na^+ , and (d) K^+ .

within Nafion increases. This observation is related to point (iii). Regardless of cleaning methods, the swelling of Nafion (by increasing its water content) decreases relaxation rates and consequently favors the rotational mobility of water within Nafion. This behavior suggests therefore a change of water environment within Nafion, which could be related to the change of the Nafion structure over a wide range of water contents.^{4,7–9} Owing to the fact that Nafion is not a cross-linked membrane, it has the ability to swell. This change of volume affects the distance between ion exchange sites and also the concentration of cations and of water within Nafion. As a consequence, the presence of cations can be concealed at high water content. In other words, the presence of cations, whatever their origin, can only be detected in a confined medium. This trend will be studied in more detail in the forthcoming section.

It is noteworthy that neither the low-frequency nor the high-frequency plateaus are visible in the dispersion curves of Figure 2. Concerning the latter, it is obviously feasible to go to higher frequencies, as explained in section 2.3. Now, the low-frequency plateau may be very narrow if some particular intermolecular relaxation mechanisms occur. A way to escape from such complications is precisely to get rid of all of the intermolecular contributions. In the case of H_2O , the remedy is very simple and, as explained in the next section, relies on the proton relaxation behavior of HOD molecules, which are the nondeuterated residues of D_2O . However, this latter method is not applicable, for sensitivity reasons, to systems possessing a too low water content.

3.2. Quantitative Analysis of H_2O and D_2O Full Dispersion Curves (5 kHz–600 MHz). Theoretical Bases. The interpretation of spin relaxation rates is generally difficult because they depend on various mechanisms such as inter- and intramolecular dipolar interactions. It was reported²¹ that dispersion curves can be interpreted as a sum of contributions arising from intra- and intermolecular movements, as well as rotations mediated by translational displacements (RMTD), $R_1 = R_1(\text{intra}) + R_1(\text{inter}) + R_1(\text{RMTD})$. The latter mode can be

seen as molecular reorientation determined by displacements between surface sites of different orientations, and it generally governs the low-frequency dispersion (10^3 – 10^7 Hz).^{19,21}

Dealing with three modes of spin relaxation rates is rather complicated. As consequence, we chose in the present work to only study the intramolecular relaxation rate. In order to isolate the latter, we assumed that (i) H_2O and HOD behave similarly on the molecular scale and (ii) the RMTD process is integrated in intramolecular motions. In fact, intramolecular relaxation arises solely from the dipolar interaction between the two protons. As a consequence, the H–H vector probes all of the rotational motions affecting the water molecule. This includes, among other things, the RMTD process. Point (i) is backed up by the fact that on a micrometric scale, the self-diffusion coefficients of Nafion prepared with both types of water are alike in the range of studied water contents.²³

Considering these assumptions, we are thus able to extract the intramolecular contribution by subtracting HOD relaxation rates from H_2O relaxation rates, as illustrated by Figure 3. This is justified by the fact that the H–D dipolar interaction is truly negligible with respect to the H–H dipolar interaction. As we

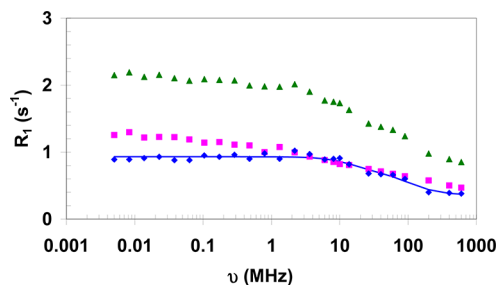


Figure 3. A typical set of experimental data for a sample prepared with H_2O (sample 6 in Table 1) (green triangles). The equivalent sample prepared with D_2O ; the data (pink squares) correspond to the residual proton of HOD. Blue diamonds: difference between the two sets of data. Continuous curve (in blue): fit of this latter difference (see the text).

are dealing with the water molecule, only the H–H dipolar interaction is involved in the interpretation of these intramolecular relaxation rates. In our study, the typical intramolecular dispersion curve (shown in Figure 3) displays, in the limit of measurement uncertainties, a plateau at low frequencies (0.005–10 MHz), confirming here that the RMTD mode is really included in the intramolecular relaxation of the water protons. These observations make us confident of our method for only extracting reliably the intramolecular dispersion rates.

In that case, the relaxation rate can be written as

$$R_1(\omega) = K_{\text{HH}} \times [4J(2\omega) + J(\omega)] \quad (3)$$

In eq 3, ω is the measurement frequency (in $\text{rad}\cdot\text{s}^{-1}$), which is proportional to the magnetic field of the NMR instrument, K_{HH} is a constant detailed below, and $J(\omega)$ is a so-called spectral density function (SDF). Whenever molecular reorientation is isotropic, the SDF has a very simple form

$$J(\omega) = \frac{2\tau_{\text{C}}}{1 + \omega^2\tau_{\text{C}}^2} \quad (4)$$

τ_{C} is the so-called correlation time that describes the molecular reorientation. It can be viewed as the time required for a rotation by an angle of 1 rad.

Moreover, the linear combination of SDF in eq 3 can be approximated by²⁴

$$4J(2\omega) + J(\omega) \approx 5J(\sqrt{3}\omega) \quad (5)$$

With these conventions, the constant K_{HH} is

$$K_{\text{HH}} = \left(\frac{3}{20}\right) \left(\frac{\mu_0}{4\pi}\right)^2 \frac{\gamma_{\text{H}}^4 \hbar^2}{r_{\text{HH}}^6} \quad (6)$$

μ_0 is the vacuum permeability, γ_{H} is the proton gyromagnetic ratio, \hbar is the Planck constant divided by 2π , and r_{HH} is the distance between the two protons in the water molecule.

In the present context, we expect several types of water, at least free (bulk) water and bound water.²⁵ It can be noticed that the correlation time of bulk water is so short (around 3 ps) that its contribution to the global relaxation rate lies in the extreme narrowing regime ($\omega^2\tau_{\text{C}}^2 \ll 1$). This evidently entails no frequency dependency. Assuming that the reorientation of the H–H vector can be considered as isotropic for any type of water, we can write the global relaxation rate as

$$R_1(\omega) = A_0 + \sum_{i=1}^n \frac{A_i}{1 + \omega^2\tau_{\text{C}_i}^2} \quad (7)$$

where n is the number of bound water types (supposed to be outside of the extreme narrowing regime). In eq 7, τ_{C_i} is an effective correlation time equal to $3^{1/2} \times \tau_{\text{C}_i}^{\text{true}}$ (see eq 5). Denoting by p_i the proportion of water type i , the coefficients in eq 7 have the following meaning

$$A_0 = (1 - \sum_{i=1}^n p_i) K_{\text{HH}} (10\tau_{\text{C}_0}) \quad (8)$$

τ_{C_0} being the correlation time for free water reorientation.

$$A_i = p_i K_{\text{HH}} \left(\frac{10}{\sqrt{3}} \tau_{\text{C}_i} \right) \quad (9)$$

It can be noticed that, some time ago, Halle²⁶ proposed a decomposition of dispersion curves in a series of Lorentzian

functions as in eq 7. As his treatment is very general, the meaning of the different correlation times is not as straightforward as it is here. This is why Halle's approach was dubbed "model free". Indeed, our τ_{C_i} 's are meaningful because we are dealing exclusively with an intramolecular dipolar relaxation mechanism.

Data Processing and Discussion. Experimental data have been processed according to eq 7 and with a procedure detailed in a previous paper.²⁷ Briefly, we start with a set of guessed τ_{C_i} 's with which A_0 and the A_i 's are determined by linear least squares (LLS). This latter procedure is quite reliable as it does not require any minimum search. With this new set of A_0 and A_i 's, new values for the τ_{C_i} 's can be calculated by nonlinear least squares (NLLS) and so on until convergence. Owing to the number of parameters to be determined, this method has proven to be much more reliable than a global nonlinear squares fit. Moreover, it can be appreciated that correlation times are exclusively deduced from the frequency variation of relaxation rates as this would be done intuitively by considering the inflection points of dispersion curves. This affords some confidence in the final results.

For each sample, data were first tentatively fitted with only one correlation time τ_{C_i} (in addition to τ_{C_0}). When the agreement between experimental data and recalculated dispersion curves did not appear satisfactory, the inclusion of a second correlation time was attempted with the hope to improve the root-mean-square deviation. This systematically succeeded for the driest samples in the four series. Figure 4

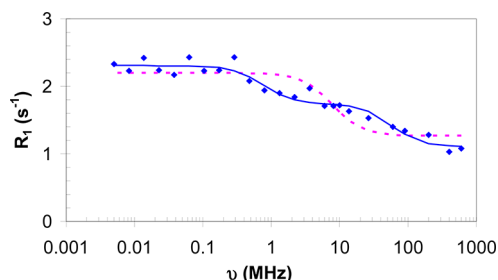


Figure 4. Experimental data of sample 1 (see Table 1) represented by blue diamonds and obtained from the difference between H_2O and HOD data. Dotted curve in pink: tentative fit with only one correlation time for bound water. Continuous curve in blue: improved fit involving two correlation times and consequently two types of bound water.

illustrates the improvement of the fit in such a situation. Here, we would like to stress that the shape of the intramolecular dispersion curves does not change even if we take into account measurement uncertainties. Concerning the latter, we consider that there are two main error sources, (i) errors arising from spin relaxation measurement ($R_1(\text{H}_2\text{O})$ and $R_1(\text{HOD})$) and (ii) errors in water content (λ), notably in the difference of water contents between samples prepared with H_2O and D_2O . Obviously, when subtracting data to get only intramolecular dispersion rates, error sources accumulate and propagate on the model fit. However, as we can see in Table 1, the propagation of errors on the model fit does not change the tendency of fit results. Typically, the variation in τ_{C_1} and τ_{C_2} is around 5–25% and 10–25%, respectively. Finally, it must be stressed that, strictly speaking, $R_1(\text{HOD})$ cannot be exactly identified as the intermolecular contribution to $R_1(\text{H}_2\text{O})$, which, in addition to

Table 1. Parameters Deduced from the Data of the 10 Investigated Samples, Which Belong to Four Families^a

samples	λ	τ_{C1} (ns)	τ_{C2} (ns)	A_0 (s ⁻¹)	A_1 (s ⁻¹)	A_2 (s ⁻¹)	p_1	p_2	$R_1(\text{free})$ (s ⁻¹)	τ_{C0} (ps)
H ⁺	1	6.3	1.6 (±0.3)	122 (±30)	1.11 (±0.07)	0.63 (±0.04)	0.0055 (±0.0015)	7.10 ⁻⁵ (±1.10 ⁻⁵)	1.12 (±0.06)	11.2 (±0.6)
	2	8.9	3.3 (±0.2)	—	0.42 —	0.43 (±0.02)	0.0019 —	—	0.42 —	4.2 —
	3	12.6	3.8 (±0.4)	—	0.32 (±0.01)	0.34 (±0.04)	0.0013 —	—	0.32 (±0.01)	3.2 (±0.01)
H ⁺ –Na ⁺ –H ⁺	4	5.9	1.4 (±0.1)	15 (±1)	0.34 (±0.01)	0.53 (±0.02)	0.0056 (±0.0003)	0.0005 (±0.0001)	0.34 (±0.02)	3.4 (±0.1)
	5	8.7	2.0 (±0.1)	—	0.34 (±0.01)	0.60 (±0.01)	0.0043 (±0.0002)	—	0.34 (±0.01)	3.4 (±0.1)
	6	12	2.0 (±0.2)	—	0.40 (±0.01)	0.52 (±0.02)	0.0038 (±0.0003)	—	0.40 (±0.01)	4.0 (±0.1)
Na ⁺	7	4.9	3.1 (±0.3)	221 (±20)	1.28 (±0.01)	4.12 (±0.12)	0.0194 (±0.0013)	0.0002 —	1.30 (±0.01)	12.9 (±0.4)
	8	11.2	1.3 (±0.1)	—	0.47 (±0.02)	0.61 (±0.02)	0.0066 (±0.0001)	—	0.47 (±0.02)	4.8 (±0.2)
K ⁺	9	3.5	13 (±3)	423 (±42)	1.5 (±0.4)	14.9 (±0.9)	0.0161 (±0.0043)	0.0009 (±0.0001)	1.5 (±0.4)	15.2 (±3.8)
	10	6.0	1.9 (±0.1)	—	0.34 —	1.42 (±0.11)	0.0107 (±0.0001)	—	0.34 —	3.4 —

^aNafion samples under acid form (H⁺), acid form with EDTA cleaning (H⁺–Na⁺–H⁺), sodium form (Na⁺), and potassium form (K⁺). τ_{C1} , τ_{C2} , and τ_{C0} in this table are obtained from the effective correlation times divided by $\sqrt{3}$.

the surface relaxivity (identical to $R_1(\text{HOD})$), may also involve dipolar interactions between protons of two different water molecules. This latter contribution, which would be proportional to the water proton density and inversely proportional to the diffusion coefficient,^{19,21} is evidently not accounted for in our analysis. However, owing to the weak water concentration and to the large magnitude of surface relaxivity, it is going to be negligible. This is further confirmed by the appearance of dispersion curves corresponding to the $R_1(\text{H}_2\text{O})$ intramolecular contribution (see, for example, Figure 3). These curves are, as expected, perfectly horizontal at low frequency.

In all cases, τ_{C0} is deduced from A_0 (see eq 8), and p_1 from A_1 (see eq 9). Results are gathered in Table 1. There is not much to say about τ_{C0} , which is close to the correlation time of bulk water except for some of the driest samples. The difference between sample 1 and sample 4 can be explained by the presence of extra cations in sample 1 (not treated with EDTA), the hydration of these extra cations lowering the water reorientation. This feature was already mentioned in section 3.1. A similar explanation can be put forward for samples 7 and 9, the relative amount of hydration water around the cation being more important than that for samples 8 and 10. An alternative (or complementary) explanation would be that samples 7 and 9 are the driest ones, thus with reduced space for free water.

At most, two correlation times (outside of the extreme narrowing regime) are detected. As a matter of fact, the large correlation time (τ_{C2}) is only involved in dry samples and corresponds to a very tiny amount of water. This will be discussed later. The other correlation time (τ_{C1} in Table 1) is on the order of a few nanoseconds and can be reasonably attributed to a solvation layer of the Nafion membrane. The only exception concerns sample 9 for which a correlation time of more than 13 ns has been found. This value can be explained by the low water content ($\lambda = 3.5$) entailing a reduced space allowed for water, and it could be due to the intermolecular water–water dipolar relaxation, which is not removed after subtracting HOD relaxation rates from H₂O relaxation rates. However, owing to the water content and as already discussed, this is rather unlikely.

It must be emphasized that for 9 samples out of 10, we obtain very consistent results, which allows us to characterize confidently this solvation layer. This consistency is confirmed by examining the p_1 values, which, as expected, always decrease when λ increases. These p_1 values are very weak and represent at most 2% of the total water amount. We turn now to the largest correlation time, τ_{C2} , which is roughly 2 orders of magnitude larger than τ_{C1} . This correlation time is found only in dry samples and is associated with an amount of water p_2 a hundred times smaller than p_1 . These considerations suggest that a small number of SO_3^- sites at the surface of the polymeric chains are able to sequester a hydrated cation. Indeed, the large difference of τ_{C2} for samples 1 and 4 can be simply explained by the extra cations that exist in sample 1 and are removed in sample 4 by the EDTA treatment, as has been already observed. Now, concerning the three samples treated with EDTA, namely, samples 4, 7, and 9, we can observe that τ_{C2} increases with the van der Waals radius. This indicates that we are very likely dealing with water molecules that surround

the cation and that the motion of the hydrated cation is restricted according to its size.

4. CONCLUSION

Two important properties concerning the treatment of the Nafion membrane have been revealed and evidenced. The first one is the influence on water behavior and mobility of unwanted cations (probably divalent) that are removed by EDTA. Concerning the water behavior and mobility, we have also shown that the nature of the counteranion can be of prime importance. These findings have been clarified and quantified by a new methodology that rests on the comparison between samples prepared with H₂O and D₂O. In this latter case, the residual proton of HOD allows us to sort out the intermolecular contribution to the spin relaxation of water protons and thus derive the pure intramolecular contribution. It turns out that in the case of water, the only relaxation mechanism governing this intramolecular contribution is simply the H–H dipolar interaction. As a consequence, the analysis of dispersion curves becomes straightforward. This analysis told us that there could exist two types of bound water. The first one is common to all samples and corresponds to the expected bound water. Conversely, the second one is only found in the driest samples and corresponds to a considerably reduced mobility. The proportion of this type of water is very weak for the samples investigated in this work but should become more important for samples with a very low water content. Such samples could actually be studied with more sensitive instrumentation, especially at very low frequencies.

AUTHOR INFORMATION

Corresponding Author

* E-mail: Feina.Xu@univ-lorraine.fr. Telephone: (33) 3 83 59 55 59.

Notes

The authors declare no competing financial interest.

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