

Self-Diffusion of a Chemical Warfare Agent Simulant and Water in Nafion by Pulsed Field Gradient NMR

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Dedicated to Prof. Dr. rer. nat. Jörg Kärger on the occasion of his 80th birthday

Pulsed field gradient (PFG) NMR at high magnetic field was used to study microscopic diffusion of dimethyl methyl phosphonate (DMMP), a common chemical warfare agent (CWA) simulant, and water in Nafion membranes. PFG NMR measurements were performed for a broad range of molecular displacements. The self-diffusivities were measured as a function of the DMMP concentration for several fixed water concentrations. The measured data suggest that DMMP and water diffuse in different regions of Nafion. While water mostly diffuses in hydrophilic regions of the membrane, viz. water channels, DMMP diffusion is mostly limited to interfacial perfluoroether regions between these water channels and the semi-crystalline matrix.

Keywords: Chemical warfare agents, Diffusion, Ionomers, Nafion, PFG NMR

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1 Introduction

Perfluorosulfonic acid (PSA) polymer membranes such as the commercially available Nafion are among the most promising materials in a wide variety of potential or current applications including fuel cells [1–4], water desalination processes [5], chemical sensing [6, 7], and selective capture/immobilization of chemical warfare agents (CWAs) [8–10]. Molecular diffusion plays an important role in these applications. However, a detailed fundamental understanding of a relationship between microscopic diffusion of different types of molecules and structural properties of Nafion membranes is still under development. In the presence of water, the Nafion structure exhibits a continuous hydrophobic semi-crystalline matrix made of a backbone of polytetrafluoroethylene and interfacial perfluoroether (PFE) regions with sulfonic head groups [11–16]. These sulfonic groups can form hydrophilic channels available for water diffusion, viz. water channels. Our previous work has provided strong evidence of independent diffusion pathways for water and acetone within the Nafion polymer [17, 18]. The presence of the interfacial PFE regions has been recognized as a key factor to understanding transport behavior in Nafion for advanced applications. Numerous molecular dynamics (MD) simulations of diffusion of water and small organic molecules contributed to understanding microscopic molecular diffusion through PSA membrane systems [3, 19–22]. However, a microscopic diffusion of organic mole-

cules larger than acetone remains mostly unexplored by both computational and experimental approaches. This leaves a gap in understanding transport properties of Nafion and other PSA membranes. This gap hinders progress in formulation and processing of PSA polymers aiming to develop and optimize new applications that involve intra-polymer diffusion.

In this work we applied pulsed field gradient (PFG) NMR to study diffusion of CWA simulant dimethyl methyl phosphonate (DMMP) and water in Nafion in the same manner as in earlier studies of Professor Jörg Kärger targeting an understanding of sorbate diffusion in zeolites and other microporous solids [23]. DMMP molecules have a “Janus” structure which contains a hydrophilic head and a hydrophobic tail. Our PFG NMR studies allowed quantifying self-diffusion of DMMP and water in Nafion for a broad range of molecular displacements. The self-diffusivities of both types of molecules were measured as a function of the DMMP concentration for a few selected water

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concentrations. The analysis of the data presented below indicates that DMMP and water diffuse in different regions of Nafion. Water mostly diffuses in water channels while DMMP diffusion appears primarily limited to interfacial PFE regions between these water channels and the semi-crystalline matrix. Such separation of diffusion pathways suggests approaches may exist for a selective capture of CWA (e.g., by reacting with selectively imbibed reagents) while allowing water to diffuse uninhibited. To our knowledge, this is the first work in which the microscopic self-diffusion coefficients of relatively large organic molecules have been quantified in Nafion experimentally.

2 Experimental Methods

2.1 Sample Preparation

Nafion 117 (Fuel Cell Store) was purified in the following manner. The membrane was submerged in 5 % hydrogen peroxide solution at 363 K for 1 h to remove impurities. Immediately following, the membrane was washed with DI water and immersed in 0.5 M sulfuric acid solution at 363 K for 1 h, in order to fully protonate the membranes. The membrane was then washed again with DI water and dried in the hood for 12 h at ambient temperature. To prepare samples for NMR studies, DMMP and water loading of the membrane were done using two separate procedures. The first of these was that roughly 120 mg of pre-cleaned membrane was placed into a 500 mL round bottom flask where the membrane was equilibrated with the DMMP and water vapors at saturation vapor pressures corresponding to the following temperatures: 294 K, 323 K, and 343 K. The DMMP and water loaded membrane was then rolled and placed into a medium-wall 5 mm NMR tube (Wilmad-Lab-Glass) for NMR measurement. The NMR tube was sealed to prevent changes in the sorbate concentrations. The second method of sample preparation is as follows. Roughly 120 mg of pre-cleaned Nafion membrane was placed into a medium-wall 5 mm NMR tube (Wilmad-LabGlass) and attached to a custom vacuum manifold to degas and remove water at 60 mTorr and 298 K for 4 h. Following this, a calculated amount of DMMP was added via a syringe and allowed to absorb into the membrane. Desired amounts of deionized water were added to the membrane via cryogenically condensing water vapor from the calibrated volume of the vacuum system using liquid N₂. Upon loading, the samples were flame-sealed and left to equilibrate for at least 24 h at 298 K. Our NMR measurements observed no systematic differences in result between the two loading methods when the same, within uncertainty, DMMP and water intra-membrane concentrations were reached.

Water and DMMP concentrations in Nafion were estimated using a commonly employed correlation between the area under the NMR spectrum and the corresponding number of molecules in a sample. This approach has been con-

firmed as valid for water and acetone inside Nafion in our previous studies [17, 18]. For this work, the area under the line approach was also successful in estimating intramembrane concentrations of DMMP and water according to these observations: (i) DMMP and water have no overlapping lines in the recorded ¹H NMR spectra, and (ii) our ¹H PFG NMR diffusion studies indicated that no bulk liquid water or DMMP was present outside the membranes in our sealed samples. The proportionality factor between the area under the lines for each sorbate and the corresponding concentrations was determined based on the measurements of the NMR spectra for known amounts of each molecule, as in our previous work [17, 18].

2.2 NMR Measurements

¹H NMR diffusion measurements were performed on a 17.6 T Bruker BioSpin wide-bore spectrometer. For ¹H PFG NMR measurements on this spectrometer, the Diff50 diffusion probe with a GREAT60 gradient amplifier was employed to generate magnetic field gradients up to 20 T m⁻¹. Measurements covered a large range of diffusion times (*t*) between 40 ms and 4 s. This work employed the 13-interval bipolar PFG NMR sequence with longitudinal eddy current delay [24, 25]. *T*₁ NMR relaxation measurements were done using the standard inversion recovery sequence, and *T*₂ measurements via the Carr-Purcell-Meiboom-Gill (CPMG) pulse sequence. The *T*₁ times for water and DMMP were equal to ~0.3 s and ~2 s, respectively. The *T*₂ times for water and DMMP were about 60 ms and 350 ms, respectively. The relatively short *T*₁ NMR relaxation time of water in these samples made it prohibitively difficult to measure water diffusion by PFG NMR for diffusion times larger than ~0.6 s for most samples.

Self-diffusion data were obtained through measurement of proton PFG NMR attenuation curves. These curves present change in the normalized PFG NMR signal (Ψ) as a function of an increasing amplitude (*g*) of the applied magnetic field gradient, with all other experimental parameters held constant. In the case of normal diffusion with a single self-diffusion coefficient (*D*), PFG NMR attenuation curves are expected to follow the following relation [23, 24]

$$\Psi = \exp(-q^2 t D) \quad (1)$$

where $q = 4\pi\gamma_{\text{nucleus}}\delta$, δ is the effective duration of a single magnetic field gradient pulse, and γ_{nucleus} is the gyromagnetic ratio of a particular type of nuclei used in the experiment. In the case when there are two ensembles of the same species diffusing with separate self-diffusion coefficients *D*₁ and *D*₂ the signal attenuation can be re-written as

$$\Psi = p_1 \exp(-q^2 t D_1) + p_2 \exp(-q^2 t D_2) \quad (2)$$

where *p*₁ and *p*₂ are the ensemble fractions corresponding to the diffusivities *D*₁ and *D*₂, which are recorded in the

PFG NMR measurement. To calculate values of the mean square displacement (MSD) for any particular ensemble or the type of molecules with the self-diffusivity D , the Einstein relation for three-dimensional diffusion was used [23]

$$\langle r^2 \rangle = 6Dt \quad (3)$$

The ^1H NMR spectra of water and DMMP in Nafion 117 membranes consisted of one line for water, at a chemical shift between 7 and 8 ppm (i.e., it changed depending on the water concentration), and two peaks for DMMP, a larger peak at roughly 4 ppm and a smaller peak at around 1 ppm. Diffusion and relaxation measurements on each DMMP peak showed no difference in the results for relaxation times and self-diffusivities. All reported NMR measurements were performed at 296 K.

3 Results and Discussion

3.1 Self-Diffusivities as a Function of Diffusion Time and Root MSD

Fig. 1 presents examples of ^1H PFG NMR attenuation curves for DMMP (A) and water (B) in Nafion membranes at 296 K. In Fig. 1A, the attenuation curves appear as straight lines, which correspond to monoexponential dependencies in agreement with Eq. (1). For DMMP, the attenuation data in Fig. 1A clearly coincide over the entire range of the diffusion times used. This demonstrates a self-diffusivity that, within uncertainty, is independent of diffusion time. Self-diffusion coefficients are presented as a function of root MSD (RMSD) in Fig. 2. Values of RMSD were obtained using the Einstein relation (Eq. (3)). As expected from the attenuation plot discussed above, the DMMP diffusivity is independent of RMSD across the entire measured range of displacements (Fig. 2).

As has been the case in our previous measurements of water in Nafion loaded with water/acetone mixtures

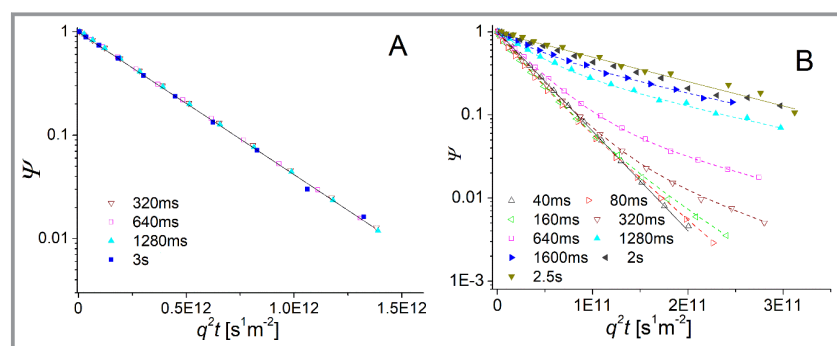


Figure 1. Examples of ^1H PFG NMR attenuation curves for DMMP (left) and water (right) in Nafion membranes loaded with DMMP and water at 296 K. The intramembrane concentrations of DMMP and water were 1.0 mmol g^{-1} and 2.7 mmol g^{-1} , respectively. Solid lines represent best fit lines using Eq. (1). Dotted lines correspond to the best fit using Eq. (2).

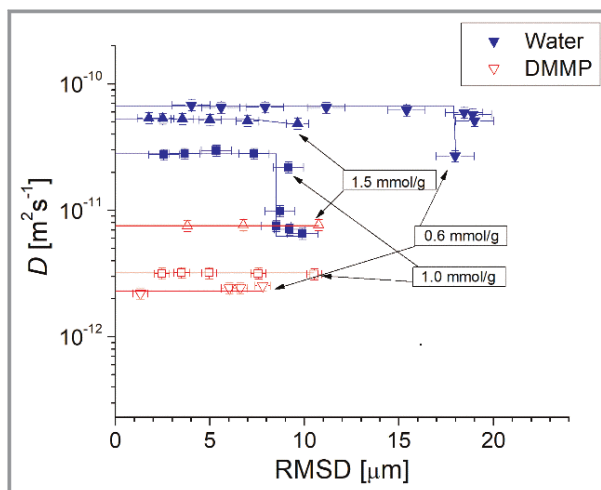


Figure 2. Dependence of the measured self-diffusivities of DMMP (red points) and water (blue points) on root MSD in Nafion membranes at 296 K for varying DMMP concentrations (indicated in figure). Water concentration was held constant at 2.7 mmol g^{-1} . Solid lines are guidelines shown as visual aids.

[17, 18], the attenuation curves measured for water (Fig. 1B) are a stark contrast to those of co-diffusing organic molecules. For all studied in this work DMMP concentrations the water attenuation curves demonstrate a monoexponential behavior and coincidence for different diffusion times only in the limit of short diffusion times $\leq 80 \text{ ms}$ (regime 1). At larger diffusion times, viz. between $\sim 160 \text{ ms}$ and $\sim 1.6 \text{ s}$ (regime 2), clear deviations from the monoexponential behavior and some dependence on the diffusion time are observed (Fig. 1B). To quantify the water PFG NMR diffusivities for the latter diffusion times only the initial part of the attenuation curve (where no deviations from the monoexponential behavior are observed) [17, 18, 23, 26] was fitted to Eq. (1) for each measured diffusion time. Fig. 2 shows all water self-diffusivities plotted as a function of RMSD for different DMMP concentrations used in our study and the water concentration of 2.7 mmol g^{-1} .

For the DMMP concentration of 1.0 mmol g^{-1} , a third regime in the limit of the largest diffusion times used ($1.6\text{--}2.5 \text{ ms}$) was observed. This regime is defined by a coincidence of the water attenuation curves and an essentially monoexponential shape of these curves. In complete analogy with our previous data for acetone diffusion in Nafion loaded with water/acetone mixtures [17, 18], it is expected that such third regime occurs for all other DMMP concentrations in the limit of long diffusion times. However, the relatively short proton T_1 NMR relaxation times of water in the measured samples prevented an observation of the third regime for all

other DMMP concentrations. The explanations of all three regimes for water diffusion is presented in the next section.

3.2 Explanation of the Dependence of Water Self-Diffusivity on Diffusion Time and Root MSD

Protons, which enter Nafion as parts of water molecules, can diffuse inside Nafion as part of their parent water molecule, but can also diffuse as other species, such as SO_3H^+ and H_3O^+ [27, 28]. This is due to proton exchange processes that are expected to occur in Nafion. Our PFG NMR measurements were performed on the millisecond time scale, which is expected to be much longer than the time scale of these proton exchange processes [27, 28]. Therefore, these exchange processes are not valid explanations for the observed time dependence of our PFG NMR data for water [17, 18].

Our previous PFG NMR studies [17, 18] of water diffusion in Nafion have discussed the observed time dependence of the PFG NMR data for water, which were analogous to those reported in the current work, in the context of water diffusing along water channels that are not fully interconnected in Nafion membrane. The diffusion data were explained by the existence of micrometer-sized domains inside Nafion in which these channels are interconnected for water to diffuse. The water diffusion in the limit of short diffusion times discussed above corresponds to the time- and RMSD-independent water self-diffusivities inside such domains (regime 1). These domains are separated by regions of a reduced water concentration. Such regions act as transport barriers for water diffusion [17, 18]. The barriers lead to decreasing water self-diffusivities with increasing diffusion time and RMSD at larger diffusion time and RMSD values when water molecules start encountering the barriers (regime 2). In the limit of largest diffusion times and RMSDs (regime 3) the water diffusion process is expected to involve crossing one or more transport barriers which leads again to the time- and RMSD-independent water self-diffusivities. Such diffusion regime was indeed observed for the DMMP concentration of 1.0 mmol g^{-1} (Fig. 2). As discussed above, the short T_1 NMR relaxation time of water prevented an observation of this regime for other studied DMMP concentrations. It is important to note that no influence of the transport barriers was observed for the diffusion of DMMP, even when the measurements were performed for essentially the same ranges of RMSD for both types of molecules (see the data for 1.0 mmol g^{-1} in Fig. 2). This observation points out that the diffusion pathways of water and DMMP are different under the conditions of co-diffusion of both types of molecules in Nafion.

3.3 Self-Diffusivities of Water and DMMP as a Function of DMMP Concentration

Fig. 3 presents DMMP and water self-diffusivities as a function of changing DMMP concentration. The data for water correspond to the limit of short diffusion times when there is no influence of the transport barriers discussed above on the diffusion process. The smallest water concentration corresponds to the case of no added water measured in the sample. In this case, the water concentration is equal to the residual water concentration in Nafion after our sample

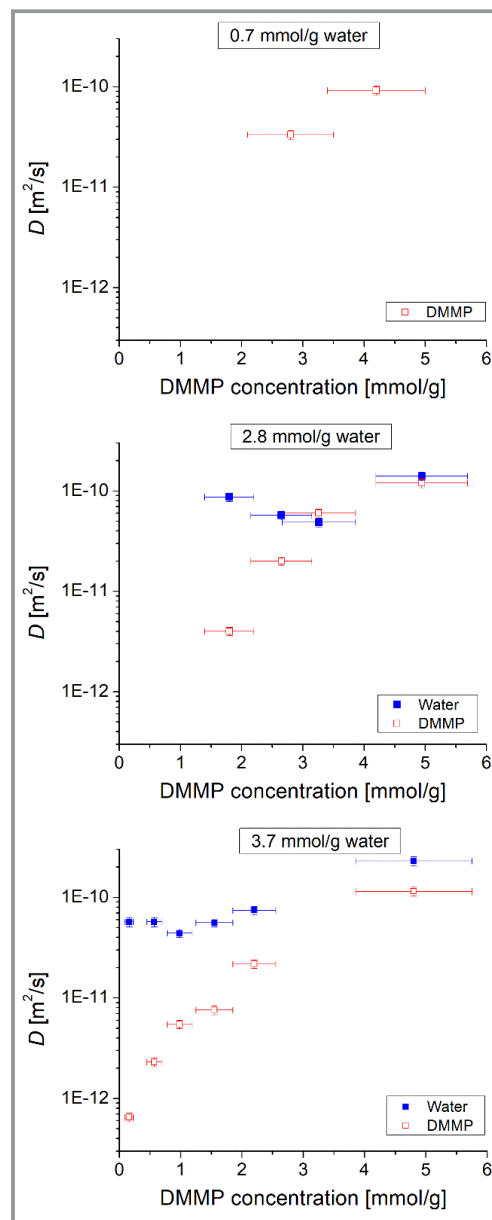


Figure 3. Self-diffusivities of water in the limit of short diffusion times (red squares) and DMMP (blue squares) measured as a function of DMMP concentration in Nafion membranes at 296 K. The PFG NMR water signal could not be measured for the smallest water concentration of 0.7 mmol g^{-1} .

preparation and water removal procedure. The data in Fig. 3 highlight that DMMP concentration within the Nafion membrane has very little effect on the diffusion of water within the membrane. At the same time, there is a much stronger dependence of the DMMP concentration on the DMMP self-diffusivity. This is indicative that water and DMMP are diffusing in different regions of the polymer. While water is known to diffuse in the domains of interconnected water channels [17, 18], DMMP likely localizes itself in the PFE interfacial regions of the polymer, similarly to acetone and other less polar organic molecules. Such localization has been observed in previous MD simulations [8]. No self-diffusion coefficients were reported, however, in this MD study. The results reported in this section support the conclusion in Sect. 3.2 about different diffusion pathways of water and DMMP in Nafion.

3.4 Quantifying Permeance of Boundaries of Domains of Interconnected Water Channels

As discussed in Sect. 3.2, the dependence of the water self-diffusivity on diffusion time and RMSD can be explained by the existence of transport barriers at the boundaries of the domains of interconnected water channels. The measured PFG NMR diffusion data for the water and DMMP concentrations indicated in Tab. 1 allowed us to estimate average sizes of the domains of interconnected water channels (N), and the permeance of the domain boundaries, with these boundaries being regions of low water mobility separating neighboring domains. For all other studied water and DMMP concentrations, short T_1 NMR relaxation times for water prevented us from measuring the diffusion time dependent attenuation curves in a sufficient range of diffusion times to perform such estimates. As discussed in our prior studies of diffusion in Nafion, N can be estimated as the characteristic RMSD value at which a substantial decrease of the water self-diffusivity with increasing RMSD occurs [17, 18]. The values of N are shown in Tab. 1. The permeance of the domain boundary (P) was estimated under the assumption that diffusion of water in the limit of long diffusion times is hindered by two transport resistances in series. The first of these corresponds to diffusion within the interconnected water channel domains, and the second

corresponds to the permeance of boundaries of such domains [17, 18, 23, 29, 30].

$$\frac{1}{D_\infty} = \frac{1}{D_0} + \frac{1}{NP} \quad (4)$$

where D_0 and D_∞ are the time independent self-diffusivities in the limit of small and large RMSDs and corresponding diffusion times, respectively. This approach was previously introduced and applied by Jörg Kärger and others for studies of diffusion in zeolites and other microporous solids [23]. For the DMMP concentration of 0.6 mmol g^{-1} for which the transition to regime 3 discussed above was not directly observable, D_∞ was estimated as the slower diffusivity from the biexponential fitting of the water attenuation curves using Eq. (2). The values of P obtained by using Eq. (4) are shown in Tab. 1.

Values for P can also be estimated using the PFG NMR tracer exchange approach introduced by Jörg Kärger [23]. This approach was applied in the same manner as in our previous studies of water diffusion in Nafion [17, 18]. Briefly, the PFG NMR tracer exchange approach describes deviations from the monoexponential attenuation behavior by assuming two molecular ensembles (Eq. (2)), each with different self-diffusivities (D_1 and D_∞) and the corresponding PFG NMR signal fractions (p_1 and $p_\infty = (1 - p_1)$) [23]. During the diffusion time used in the PFG NMR experiment, molecules remaining inside the same domain of interconnected water channels correspond to the PFG NMR signal fraction p_1 and the larger self-diffusivity D_1 . The ensemble of molecules that corresponds to diffusion through more than one domain is characterized by the smaller self-diffusivity D_∞ and the signal fraction $(1 - p_1)$. Since there is no distribution over T_1 and T_2 NMR relaxation times for water, the PFG NMR signal fractions should coincide with the true molecular fractions of each ensemble. As a result, the fraction of molecules (γ) which crosses over a domain boundary and leaves the original domain should be equal to $(1 - p_1)$. The diffusion time dependence of γ represents a tracer exchange curve, which can be interpreted like in traditional tracer exchange experiments between confining domains and their surroundings [23, 29]. Fig. 4 presents the dependency of $p_1 = (1 - \gamma)$ on diffusion time for one DMMP concentration equal to 1 mmol g^{-1} for

Table 1. Average size of domains of interconnected water channels, permeance of the domain boundaries, and time constant of molecular exchange for these domains in Nafion loaded with DMMP and water.

DMMP conc. [mmol g ⁻¹]	H ₂ O conc. [mmol g ⁻¹]	Temp. [K]	N [μm]	$P \times 10^6$ [m s ⁻¹] using Eq. (4)	R [μm]	τ_{ex} [s]	$P \times 10^6$ [m s ⁻¹] using Eq. (5)
0.6 ± 0.1	2.8 ± 0.5	296	18 ± 4	3.0 ± 0.6	—*	—*	—*
1.0 ± 0.2	2.9 ± 0.5	296	8.5 ± 2	1.0 ± 0.3	4.3 ± 1.0	1.4 ± 0.3	1.1 ± 0.2

*For this sample Eq. (4) can be used to estimate P , but Eq. (5) cannot because the low signal-to-noise ratios in the PFG NMR measurements did not allow us to measure the signal fraction of the slower diffusing molecules in regime 2 as a function of diffusion time for a sufficiently large range of diffusion times.

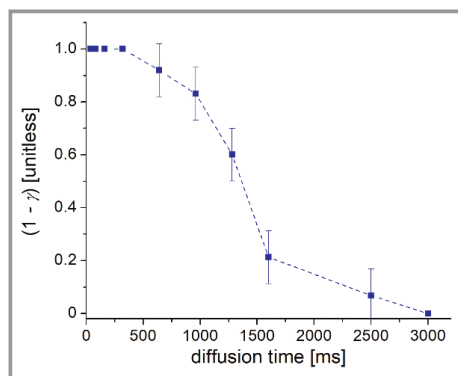


Figure 4. Fraction of water molecules ($1 - \gamma$) which remain in the same domain of interconnected water channels after a certain diffusion time plotted as a function of this diffusion time for Nafion membranes at 296 K loaded with 3.0 mmol g^{-1} water and 1.0 mmol g^{-1} DMMP.

which a transition to the third diffusion regime of the time- and RMSD-independent self-diffusivity in the limit of large diffusion times and RMSDs was observed.

The area under the dependency yields the first statistical moment. This quantity is equivalent to the time constant of molecular exchange (τ_{ex}), or the mean lifetime of a molecule within a certain domain. This quantity is related to boundary permeance by [23, 29]

$$\tau_{ex} = \int_{t=0}^{\infty} (1 - \gamma) dt = \frac{R^2}{15D_0} + \frac{R}{3P} \quad (5)$$

under the assumption that domains are spherical with radius R (Tab. 1). Eq. (5) arises from the addition of the first moment $R^2/(15D_0)$ associated with transport resistance due to diffusion within a domain, and the corresponding first moment $R/(3P)$ associated with the resistance of the domain boundaries [23, 29].

Values of the radius of spherical domains R were estimated in the following manner. It is understood that the effect of confinement from the domain boundaries on self-diffusion within a domain can be presented as a function of the surface-to-volume ratio of these domains, as a first approximation [23, 29]. This function is not influenced by the shape of the domain itself. This lack of sensitivity to domain shape can be justified under the realization that the probability for a molecule to be at the domain surface, under the condition of a uniform intra-domain concentration of diffusing molecules, can only be controlled by surface-to-volume ratio. For spherical domains with radius R and cubic domains of side length N , the value of the surface-to-volume ratio would be identical when $R = N/2$, so the value of R was estimated as $N/2$. Under this estimate, the second term in Eq. (5) $R/(3P)$ was consistently larger than the first term $R^2/(15D_0)$. Therefore, an estimate of the domain boundary permeance using Eq. (5) was obtained where the contribution of the $R^2/(15D_0)$ term was taken

into account, but found to be insignificant. Within uncertainty, the two methods of estimating P are in a good agreement for the DMMP concentration of 1.0 mmol g^{-1} (Tab. 1), which confirms the validity of our estimations. For the lower DMMP concentration of 0.6 mmol g^{-1} (Tab. 1) we could not use the PFG NMR tracer exchange approach (Eq. (5)) to estimate the value of P due to the low signal-to-noise ratios in the PFG NMR measurements, which did not allow obtaining the signal fraction of the slower diffusing molecules in regime 2 as a function of diffusion time for a sufficiently large range of diffusion times. From Tab. 1, we note that increased DMMP concentration in the membrane from 0.6 mmol g^{-1} to 1.0 mmol g^{-1} reduces water permeance through the domain boundaries.

4 Conclusions

To our knowledge, this work represents the first microscopic measurements of diffusion of a CWA simulant in PSA polymers. The results of the study indicate that water and DMMP, and likely other CWAs and CWA simulants with similar structures, mostly diffuse in different local environments of Nafion. While water mostly diffuses in hydrophilic regions of Nafion, i.e., in domains of interconnected water channels, DMMP diffusion is mostly restricted to PFE interfacial regions of Nafion between these water channels and the semi-crystalline matrix. This knowledge increases the potential for use of Nafion and/or other PSA polymers to capture CWAs by targeted polymer functionalization of selected polymer regions with CWA traps, while still allowing water diffusion to occur uninhibited through water channels.

Acknowledgments

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Symbols used

D_i	$[\text{m}^2 \text{s}^{-1}]$	self-diffusivity in biexponential fittings of PFG NMR attenuation curves for ensemble i
D_0	$[\text{m}^2 \text{s}^{-1}]$	self-diffusivity of measured species in the limit of short diffusion times
D_∞	$[\text{m}^2 \text{s}^{-1}]$	self-diffusivity of measured species in the limit of long diffusion times
g	$[\text{T m}^{-1}]$	magnetic field gradient strength

N	[m]	estimated size of domains of interconnected water channels in Nafion
P	[m s ⁻¹]	permeance of the boundaries of domains of interconnected water channels in Nafion
p_i	[-]	PFG NMR signal fractions in biexponential fittings of PFG NMR attenuation curves for ensemble i
q	[m ⁻¹]	parameter equal to $4\gamma_{\text{nucleus}}\delta$
$\langle r^2 \rangle$	[m ²]	mean squared displacement
R	[m]	effective radius of spherical domains in the PFG NMR tracer exchange experiment
t	[s]	diffusion time
T_1	[s]	NMR longitudinal relaxation time
T_2	[s]	NMR transverse relaxation time

Greek letters

γ	[-]	fraction of molecules that left an original domain after diffusion time t
γ_{nucleus}	[rad s ⁻¹ T ⁻¹]	gyromagnetic ratio of the measured nucleus
δ	[s]	effective duration of a single magnetic field gradient pulse
τ_{ex}	[s]	time constant of molecular exchange in the PFG NMR tracer exchange experiment

Abbreviations

CWA	chemical warfare agent
DMMP	dimethyl methyl phosphonate
MC	Monte Carlo
MD	molecular dynamics
MSD	mean square displacement
NMR	nuclear magnetic resonance
PFG	pulsed field gradient
PSA	perfluorosulfonic acid
RMSD	root mean square displacement

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