

# Self-Diffusion of Ions at Different Time Scales in a Porous and Charged Medium: The Nafion Membrane

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The self-diffusion coefficients of  $\text{N}(\text{CH}_3)_4^+$  ions in a cation-exchange membrane, the Nafion, have been measured at different time scales. The time range extends from the picosecond with neutron quasi-elastic scattering experiments to the second with NMR experiments and tens of seconds with radiotracer experiments. At short times, the values of self-diffusion coefficient in the membrane are equal to those in nonconfined solution; the diffusion process is governed by ion–solvent collisions. The NMR results present two different time scales: for short times ( $<1$  s), the self-diffusion coefficient depends both on time and on electrolyte concentration; for long times, these two dependencies disappear. The radiotracer method confirms the NMR results at long time scales: the diffusion does not depend on electrolyte concentration.

## 1. Introduction

Diffusion processes occur from short time scales (picosecond) until geological time scales. An interesting insight in the dynamics of condensed phases is obtained by examining the diffusion processes over different observation time scales.

In low viscosity liquids and solutions, the diffusion coefficients vary in the picosecond–nanosecond range, due to local interactions: reflection in solvent cage, electrostatic interactions, etc. The “long time” behavior is observed for times larger than 1 ns, which is the characteristic time for establishment of most relaxation processes, such as Debye’s.

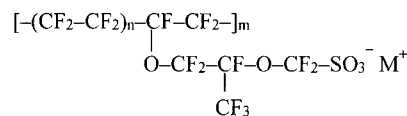
In porous media, additional interactions occur between the diffusing species and the medium. These interactions depend on the material considered. In the case of Nafion membranes, depending on the observation time, one will see mainly either the internal motion inside cavities which contain ionic solutions, or the motion from cavity to cavity and the motion through the whole membrane.

Consequently, transport in this complex medium might be characterized by several characteristic times, each one corresponding to an individual process. Thereby, the determination of these characteristic times may give valuable information about the solute–Nafion interactions. These characteristic times can be determined by using several experimental techniques with different observation times. In the present study, three experimental techniques have been used: NQES (neutron quasi-elastic scattering), NMR (nuclear magnetic resonance), and a radio-

tracer method. In a NQES experiment (with a time-of-flight spectrometer), a dynamic process can be observed during a time of the order of the picosecond. In an NMR experiment, this time is larger, as it extends from a hundred milliseconds to the second. Finally, in an experiment using radiotracers, this time is in the range 10 s to 10 min (in our case this time was about 100 s).

To our knowledge, no study has been reported on the dynamics in Nafion membrane on such a range of time scales. A few studies have been done by NQES on the diffusion of water molecules in Nafion membranes,<sup>1,2</sup> but none on the diffusion of ions. Likewise, there are few studies by NMR on the diffusion of water molecules<sup>3–6</sup> and ions.<sup>7</sup> On the contrary, many macroscopic studies (such as radiotracer methods) have been performed on water<sup>8,9</sup> diffusion and on ion<sup>10–13</sup> diffusion.

In this study, the ions were  $\text{N}(\text{CH}_3)_4^+$  ions and the porous and charged medium was the Nafion 117 membrane. The  $\text{N}(\text{CH}_3)_4^+$  ion, because of its 12 hydrogens, can be easily studied by NQES and by NMR; furthermore, this ion can be radio-labeled using  $^{14}\text{C}$ . The Nafion membranes are cation-exchange membranes that have been synthesized since the early 1960s by Dupont de Nemours. This industrial membrane is widely studied<sup>14</sup> and used<sup>15</sup> in such fields as chlor-alkali cells,<sup>16</sup> fuel cells,<sup>17</sup> the design of modified electrodes,<sup>18–21</sup> and organic synthesis.<sup>22–24</sup> This membrane is composed of a linear polymer of fluorocarbon with an anionic ending: a sulfonate group.



With  $n=6.5$  and  $100 < m < 1000$  (Nafion 117)

The most commonly accepted model is the following. The anionic groups build inverted micelles and thus form, in the

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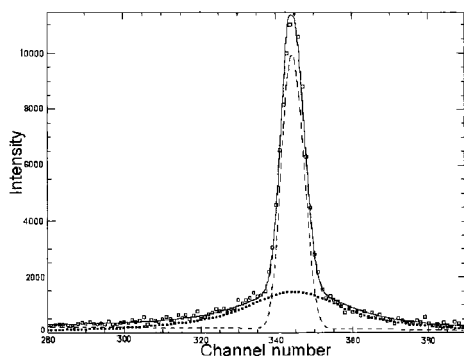
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**Figure 1.** Comparison of experimental ( $\square$ ) and calculated (line) NQES spectra for a given  $q$ . The dashed line represents the elastic scattered intensity and the filled squares the quasi-elastic scattered intensity.

hydrophobic polymer matrix, hydrophilic cavities in which an aqueous solution can penetrate. The diameter<sup>25</sup> of these cavities is about 40 Å. They are connected by small pores whose size has been estimated at 10 Å length and 10 Å diameter.<sup>26</sup> Another relevant feature of the Nafion membranes is the anionic site concentration in the hydrophilic domains: it is about 4 mol/L.

## 2. Experimental Section

**2.1. Preparation of Membranes.** Nafion membranes are known to be sensitive to previous treatments.<sup>27,28</sup> In this work, the Nafion membranes were prepared as follows: they were soaked for 2 h in 1 mol·L<sup>-1</sup> HCl, then for 2 h in 1 mol·L<sup>-1</sup> NaOH. This operation was repeated twice, and then the membranes were left for 1 h in boiling deionized water; then, they were immersed in concentrated N(CH<sub>3</sub>)<sub>4</sub>Cl solution in order to neutralize all the anionic groups with N(CH<sub>3</sub>)<sub>4</sub><sup>+</sup> ions. Finally, the membranes were equilibrated with the studied solution.

For the NQES and NMR experiments, the solutions were N(CH<sub>3</sub>)<sub>4</sub>Cl in D<sub>2</sub>O. Since the N(CH<sub>3</sub>)<sub>4</sub>Cl salt is hygroscopic, solutions were prepared with salt that had been previously dissolved in D<sub>2</sub>O and dried again in order to remove H<sub>2</sub>O molecules. For radiotracer experiments, the solutions were N(CH<sub>3</sub>)<sub>4</sub>Cl in H<sub>2</sub>O solutions.

**2.2. NQES.** The NQES experiments were performed with the time-of-flight spectrometer Mibemol at Laboratoire Léon Brillouin (CEA-CNRS Saclay, France). The samples were placed in a cylindrical cell, which was hermetically closed in order to prevent samples from drying out. The systems were thermostated at 25 °C. The studied samples were as follows: Nafion membranes equilibrated with solutions of N(CH<sub>3</sub>)<sub>4</sub>Cl in D<sub>2</sub>O at 0.5 and 2 mol/kg and N(CH<sub>3</sub>)<sub>4</sub>Cl in D<sub>2</sub>O solutions at 1, 3.5, 4.5, and 8 mol/kg.

With the aim of eliminating the contribution of the polymer to the scattered intensity, the spectrum obtained with a membrane equilibrated with Na<sup>+</sup> ions was subtracted from the spectrum obtained with a membrane equilibrated with N(CH<sub>3</sub>)<sub>4</sub><sup>+</sup> ions. The membrane neutralized by Na<sup>+</sup> was prepared in the same way as the membranes neutralized by N(CH<sub>3</sub>)<sub>4</sub><sup>+</sup> ions (see section 2.1).

The elastic and the inelastic peaks were extracted from the scattered intensity with the "fitmib" program (LLB). The elastic peak was approximated by a Gaussian and the inelastic peak by a Lorentzian. The background was supposed linear versus energy transfer. An example of fit is presented in Figure 1.

The motion that can be observed in NQES experiments depends on experimental resolution: at low resolution, fast motions are observed, while at high-resolution slow motions are observed. For N(CH<sub>3</sub>)<sub>4</sub><sup>+</sup> ion, there are three kinds of motion

from the fastest to the slowest: H rotation around C, CH<sub>3</sub> rotation around N, and N(CH<sub>3</sub>)<sub>4</sub><sup>+</sup> diffusion.

For Nafion membranes, the measurements were performed for two resolutions: 180 and 20 μeV. At 180 μeV resolution, neutron wavelength  $\lambda$  is 6 Å and the  $q$  range (where  $q$  is the wavenumber transfer) is between 0.5 and 2 Å<sup>-1</sup>; at 20 μeV resolution,  $\lambda = 10$  and 0.3 Å<sup>-1</sup> <  $q$  < 1.2 Å<sup>-1</sup>. For the N(CH<sub>3</sub>)<sub>4</sub>-Cl solutions, the measurements were performed only at 20 μeV resolution.

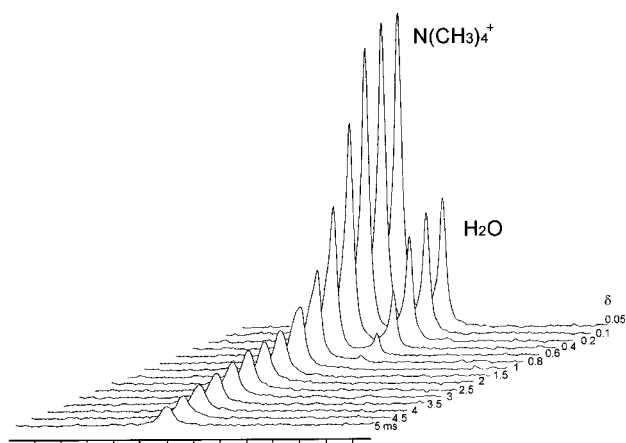
**2.3. NMR.** The NMR measurements have been performed at a temperature of 25 °C, on Nafion membranes equilibrated with solutions of 0.1, 0.5, 1, and 2 mol/kg N(CH<sub>3</sub>)<sub>4</sub>Cl in D<sub>2</sub>O.

For diffusion measurements, a piece of membrane was placed vertically (with appropriate slots) in a small container filled with tetramethylammonium chloride solution. Finally, this assembly was oriented in such a way that the membrane plane was perpendicular to the field-gradient axis. This procedure leads to the measurement of the self-diffusion coefficient in the direction perpendicular to the membrane plane. The experimental NMR method employs radio frequency field gradients.<sup>29</sup> The advantage of such a procedure lies in the immunity to internal static field gradients (necessarily present in inhomogeneous samples as those under investigation here) which may hamper diffusion measurements at long observation times when conventional static field gradients are employed.<sup>30</sup> Moreover, still in contrast with the latter, the negligible rise and fall times of radio frequency field gradients<sup>29</sup> ensure safe measurements at short observation times (diffusion intervals). Moreover, to make sure that the decrease of the apparent diffusion coefficients (observed in the systems investigated here) is not an artifact, test measurements have been performed with a solution for which the diffusion coefficient is of the same order of magnitude and should not vary with the length of the diffusion interval.

The method is now briefly outlined. A first gradient pulse (of duration  $\delta$ ) totally defocuses the nuclear magnetization (proton magnetization in the present study); after the application of a second pulse of opposite phase, refocusing would occur. However, because an interval (denoted by  $\Delta$  in the following) is allowed between the two pulses and because a gradient acts as space labeling, refocusing is not complete if the considered molecule has moved during  $\Delta$  and the final longitudinal nuclear magnetization  $M(\delta, \Delta)$  is given by

$$M(\delta, \Delta) = M_0 \exp(-\Delta/T_1) \exp(-2\delta/T_{1,2}) \exp(-\gamma^2 g_1^2 D \gamma^2 \Delta) \quad (1)$$

where  $M_0$  is the equilibrium magnetization,  $\gamma$  the proton gyromagnetic ratio,  $g_1$  the gradient magnitude,  $D$  the diffusion coefficient.  $T_1$  and  $T_2$  are, respectively, the longitudinal and transverse relaxation times, one has  $1/T_{1,2} = (1/2)(1/T_1 + 1/T_2)$ .  $T_{1,2}$  acts during the gradient pulses, whereas it is the longitudinal relaxation time  $T_1$  that produces an additional loss during the diffusion interval  $\Delta$ . This is in contrast with the classical pulsed gradient spin-echo (PFGSE) that involves  $T_2$ . It can be recalled that in systems similar to those investigated here, one has generally  $T_1$  greater or much greater than  $T_2$ ; therefore, such systems are better dealt with by the present method. The self-diffusion coefficient is generally extracted from a series of measurements involving different  $\delta$  values (in the millisecond range) with  $\Delta$  fixed (chosen in the range of the hundreds of milliseconds). In this sort of system that possesses low  $T_2$  (of the order of 10–20 ms), some care must be exercised concerning the term  $\exp(-2\delta/T_{1,2})$ , which also varies with  $\delta$ . In fact,  $T_1$  (in the range 700–950 ms) and  $T_2$  of N(CH<sub>3</sub>)<sub>4</sub><sup>+</sup> inside the



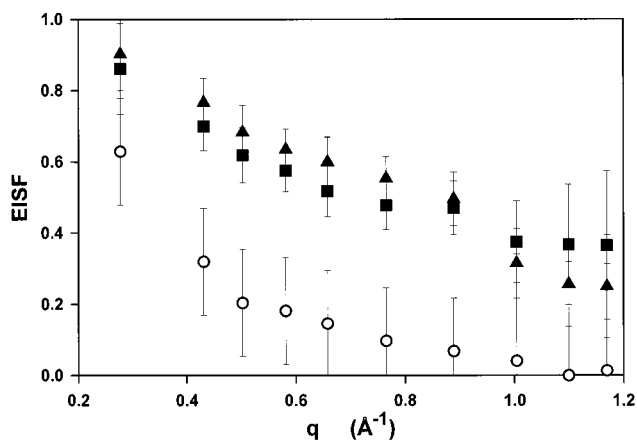
**Figure 2.** Series of NMR measurements of self-diffusion performed on the investigated systems at 100 MHz (as all experiments reported in this paper).  $\Delta$  is fixed at 200 ms. The  $\delta$  value is given for each trace. Note the fast decay of the bulk signals ( $\text{H}_2\text{O}$  and  $\text{N}(\text{CH}_3)_4^+$ ) leading to an accurate measurement of the sole  $\text{N}(\text{CH}_3)_4^+$  inside the membrane (from  $\delta = 1.5$ –5 ms).

membrane have been systematically measured by means of independent experiments in order to determine  $\exp(-2\delta/T_{1,2})$  in eq 1.

In all these experiments (diffusion or relaxation), the problem of separating different contributions has to be considered. These contributions arise from the presence in the proton NMR spectrum of (1) the species of interest, that is  $\text{N}(\text{CH}_3)_4^+$  ion inside the membrane, (2)  $\text{N}(\text{CH}_3)_4^+$  in the bulk, which appears at the same chemical shift as the latter, (3) residual  $\text{H}_2\text{O}$  whose signal may interfere with  $\text{N}(\text{CH}_3)_4^+$  peak. An interesting property is that the  $\text{N}(\text{CH}_3)_4^+$  ion in the bulk and residual  $\text{H}_2\text{O}$  possesses a self-diffusion coefficient larger by 2 orders of magnitude than the  $\text{N}(\text{CH}_3)_4^+$  ion inside the membrane. This suggests a very efficient method for eliminating the two unwanted signals. This method rests on the diffusion experiment applied with appropriate  $\delta$  and  $\Delta$  values, large enough to suppress the fast diffusing species but small enough for hardly affecting  $\text{N}(\text{CH}_3)_4^+$  inside the membrane. This feature is illustrated by the series of measurements shown in Figure 2. It thus suffices to include such a sequence prior to the classical relaxation measurement schemes (inversion-recovery for  $T_1$ , CPMG for  $T_2$ ). Concerning the diffusion measurements themselves (see again Figure 2), the first  $\delta$  values will be discarded until the bulk signals ( $\text{H}_2\text{O}$  and  $\text{N}(\text{CH}_3)_4^+$ ) have virtually disappeared.

**2.4. Radiotracers.** The radiotracer method used here is based on the rotating electrode principle. A precise description of this method has been given in a previous publication.<sup>31</sup> However, the principle can be briefly outlined: a circular piece of membrane was glued on a Plexiglas cylinder with a mastic. The cell was first immersed into an electrolyte solution of a given molality  $m$ . After a sufficient time, it was introduced into a radiolabeled electrolyte solution of the same composition. When equilibrium was reached, the cell was mounted on a rotating electrode spindle and immersed into a nonradioactive solution of molality  $m$ . Then successive aliquots of this solution were taken as a function of time. It can be noticed that the diffusion measurement is performed in direction perpendicular to the membrane plane, as in the NMR experiments.

The radiolabeled  $^{14}\text{CH}_3\text{N}(\text{CH}_3)_3^+$  species have been synthesized in the Laboratoire des Molécules Marquées (CEA Saclay, France). This synthesis was performed with  $^{14}\text{CH}_3\text{I}$  and  $\text{N}(\text{CH}_3)_3$ . Consequently, there are  $\text{I}^-$  ions in the radioactive solution,



**Figure 3.** EISF obtained with NQES spectra at 20  $\mu\text{eV}$  resolution of a 8 mol/kg  $\text{N}(\text{CH}_3)_4\text{Cl}$  solution (○) and of Nafion membrane equilibrated with 0.5 mol/kg (▲) and 2 mol/kg (■)  $\text{N}(\text{CH}_3)_4\text{Cl}$  solution.

however, in small amounts compared with the  $\text{Cl}^-$  ions of the supporting electrolyte.

The systems that have been studied with this radiotracer method are as follows: Nafion membranes equilibrated with solutions of 0.1, 0.5, 1, and 2 mol/kg  $\text{N}(\text{CH}_3)_4\text{Cl}$  in  $\text{H}_2\text{O}$ .

### 3. Results

**3.1. NQES.** The scattered intensity is composed of an elastic component that may give information on the motion geometry and an inelastic component that gives the velocity constant of the motion. The most convenient way to analyze the elastic component is to use the elastic incoherent structure factor (EISF), whose expression is<sup>32</sup>

$$\text{EISF}(q) = \frac{I_E(q)}{I_E(q) + I_I(q)} \quad (2)$$

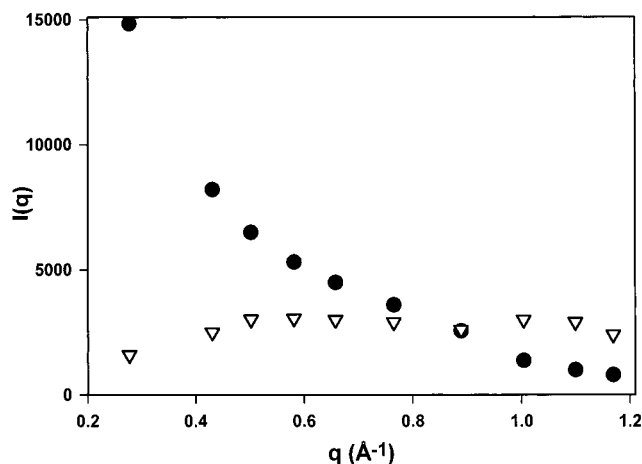
where  $I_E$  is the intensity of the elastic peak and  $I_I$  is the intensity of the inelastic peak.

Elastic incoherent scattering occurs (except at  $q = 0$ ) when the motion is confined in space. It vanishes in the case of diffusion.

The shape of the EISF obtained from the spectra at 180  $\mu\text{eV}$  indicates that the observed motion is a rotation on a sphere. An analytical expression for the scattered intensity for such motion has been given by Sears.<sup>33</sup> In this formalism the EISF is

$$\text{EISF}(q) = j_0^2(qR) \quad (3)$$

where  $j_0$  is the spherical Bessel function and  $R$  is the radius of the sphere. The radius  $R$  can then be obtained from eq 3: for  $\text{N}(\text{CH}_3)_4^+$  in Nafion membrane and in  $\text{N}(\text{CH}_3)_4\text{Cl}$  bulk solutions,  $R$  is 2.1 Å at 180  $\mu\text{eV}$ . This motion corresponds to the rotation of methyl group around N (radius of  $\text{N}(\text{CH}_3)_4^+$  2.2 Å). Unfortunately, poor statistics prevent from obtaining the rotational diffusion coefficient. As previously mentioned, by changing the resolution the observation time is changed. At higher resolution (20  $\mu\text{eV}$ ) motions slower than methyl rotation around nitrogen are expected to be observed. Then, this resolution allows observation of the diffusion process. Figure 3 presents the EISF obtained for the membranes and for a solution (8 mol/kg) at 20  $\mu\text{eV}$  resolution. For the solutions, the EISF is low (nearly zero within experimental error), which is the signifying of a diffusion. For Nafion membranes, the EISF is appreciable but does not show any particular shape. It must be pointed out that the quasi-



**Figure 4.** Neutron elastic (●) and quasi-elastic (▽) scattering intensity of  $\text{N}(\text{CH}_3)_4^+$  in Nafion membrane. Example of Nafion membrane equilibrated with 0.5 mol/kg. The sum of the elastic and the quasi-elastic intensity is not constant versus  $q$  because of a remaining contribution of elastic coherent intensity due to the polymer.

elastic intensity (see Figure 4) is constant versus  $q$  which confirms that the motion observed at  $20 \mu\text{eV}$  is the diffusion process. The important elastic intensity observed for Nafion membranes is a remaining coherent scattering due to the polymer and the ion structures. It must be noticed that the Nafion structure depends slightly on both the counterion and the electrolyte concentration. Therefore, the whole coherent elastic intensity in the quasi-elastic spectra cannot then be removed by a simple subtraction of a spectrum obtained by Nafion membrane neutralized with nonprotonated ions such as sodium. Moreover, it has been shown that the intensity scattered at small angle is greater for a membrane neutralized with  $\text{N}(\text{CH}_3)_4^+$  than with  $\text{Na}^+$  ions.<sup>34</sup> We have verified that it does not affect the quasi-elastic peak (intensity and HWHM values).

For a simple diffusion the incoherent scattering function  $S_{\text{inc}}(q, \omega)$  can be written in the following manner:<sup>35</sup>

$$S_{\text{inc}}(q, \omega) = \frac{1}{\pi} \frac{y(q)}{\omega^2 + (y(q))^2} \quad (4)$$

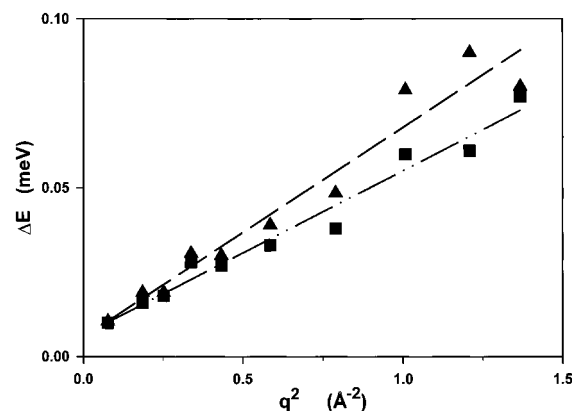
with  $\hbar\omega$  the energy transfer and  $y(q)$  the half-width at the half-maximum of  $S_{\text{inc}}(q)$ .

In the limit of small  $q$ ,  $y(q)$  becomes

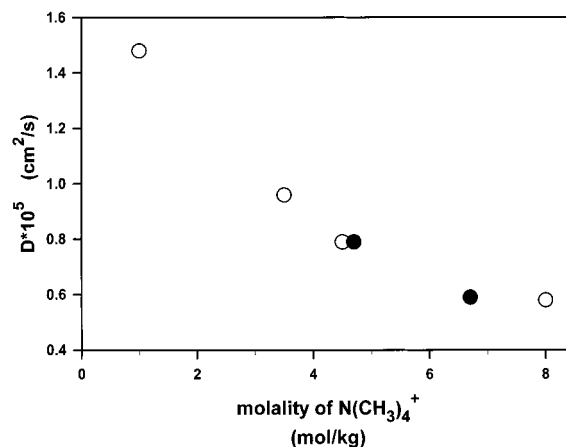
$$\lim_{q \rightarrow 0} y(q) = Dq^2 \quad (5)$$

where  $D$  is the self-diffusion coefficient.

The self-diffusion coefficients of  $\text{N}(\text{CH}_3)_4^+$  ions in solutions are obtained from a linear regression of  $y$  versus  $q^2$ . The  $20 \mu\text{eV}$  resolution corresponds approximately to an observation time of  $9 \times 10^{-11}$  s and, with a self-diffusion coefficient of about  $10^{-5} \text{ cm}^2 \text{ s}^{-1}$ , to a displacement of  $3 \text{ \AA}$ . This length is quite small as compared with Nafion cavity size (about  $20 \text{ \AA}$  radius<sup>25,34</sup>), thus allowing one to use the same model for determining the self-diffusion coefficient from NQES spectra. Furthermore, this choice is justified by the linear plot of  $y(q)$  versus  $q^2$  (Figure 5). A model of diffusion in a sphere has been developed by Volino and al.<sup>36</sup> and applied to the diffusion of water molecules in Nafion membranes.<sup>1</sup> We did not use this model in the present study for the following reasons: first, the  $\text{N}(\text{CH}_3)_4^+$  ions are located near the cavity wall and do not occupy the whole volume of cavities in contrast with water



**Figure 5.** Variation of the HWHM of the neutron quasi-elastic peak versus  $q^2$  of Nafion membrane equilibrated with 0.5 mol/kg (▲) and 2 mol/kg (■)  $\text{N}(\text{CH}_3)_4\text{Cl}$  solution.



**Figure 6.** Variation of self-diffusion coefficient of  $\text{N}(\text{CH}_3)_4^+$  in Nafion membrane (●) and in nonconfined solution (○) versus  $\text{N}(\text{CH}_3)_4\text{Cl}$  molality, as measured by NQES.

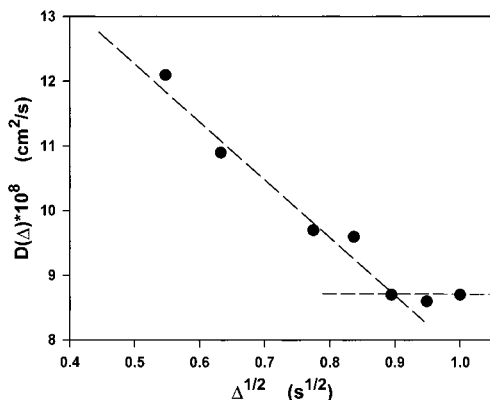
molecules; second, our experimental data can be well reproduced using eq 3 (see Figure 1). Thus, a more sophisticated model is not needed.

To compare the self-diffusion in solution and within a Nafion membrane, the molality of  $\text{N}(\text{CH}_3)_4^+$  ions in the hydrophilic domains of Nafion was measured by weighing a membrane swollen with electrolyte solution, a membrane swollen with water and a dried membrane. The values of  $D$  are plotted as a function of  $\text{N}(\text{CH}_3)_4^+$  molality (Figure 6). One can notice that the self-diffusion coefficients in the Nafion membrane fall on the curve corresponding to the self-diffusion coefficients in solution. It appears therefore that, within these time and space scales, the self-diffusion process is similar to that in nonconfined solution. Volino et al.<sup>1</sup> have observed by NQES that water molecules have the same behavior in Nafion cavities as in bulk water.

The aqueous solutions are mainly located in Nafion cavities, not in the connecting pores. Consequently, the self-diffusion observed by NQES experiments (with a time-of-flight spectrometer) is the self-diffusion which occurs in the Nafion cavities.

**3.2. NMR.** In these experiments, special care must be taken because of the low value of the diffusion coefficients to be measured (around  $10^{-7} \text{ cm}^2 \text{ s}^{-1}$ ) and of sensitivity problems. Nevertheless, the major trends, as a function of  $\text{N}(\text{CH}_3)_4^+$  concentration, could be assessed. The striking feature of the experimental results is a decrease in the measured self-diffusion coefficient (apparent  $D$ ) when the diffusion interval  $\Delta$  is





**Figure 7.** Variation of the apparent self-diffusion coefficient of  $\text{N}(\text{CH}_3)_4^+$  in Nafion membrane (●) versus the square root of the diffusion interval  $\Delta$  in NMR sequence. The two straight lines are representative of approximations valid at short and long times, respectively. Example of Nafion membrane equilibrated with 0.5 mol/kg.

increased. Such a behavior is not uncommon and reflects some restriction opposing the diffusion process. Indeed, Mitra et al.<sup>37,38</sup> have developed an appealing theory whose main features can be summarized as follows. In a porous medium and at short diffusion intervals  $\Delta$ , only those molecules in a thin layer close to the solid walls experience the effect of the latter. This leads to an apparent self-diffusion coefficient reduced by an amount proportional to the quantity of molecules in this layer which can be expressed as  $S/V$ , where  $S$  and  $V$  are the area and the volume of the pore space, respectively. More precisely, denoting by  $D_0$  the true self-diffusion coefficient, Mitra et al.<sup>37</sup> obtained

$$D(\Delta) = D_0 \left[ 1 - \frac{4}{9\sqrt{\pi}} \frac{S}{V} \sqrt{D_0 \Delta} \right] \quad (6)$$

for short observation times.

Conversely, at very long diffusion intervals  $\Delta$ , multiple reflections on the solid walls occur. Then, the details of the pore space no longer matter and one is left with only a tortuosity effect, independent of the duration of the diffusion time interval. To a first approximation one obtains

$$D(\Delta) = D_0 \alpha^{-1} \quad (7)$$

for long observation times where  $\alpha$  is the tortuosity ( $\alpha \geq 1$ ). Of course (5) and (6) represent crude approximations (with respect to the complete theory of Mitra et al.<sup>37</sup>). However, they should however be sufficient in the present context, owing to the limited number of data points and to their accuracy. The best experimental result at a representative concentration is displayed in Figure 7 along with two straight lines: one corresponds to the short time approximation, which provides  $S/V$  (from the slope) and  $D_0$  (from the intercept); the other one, which should be horizontal, represents diffusion coefficients at long times (which become independent of  $\Delta$ ) and yields the tortuosity,  $D_0$  being known from the initial behavior. All available experimental data are gathered in Table 1. The analysis was performed in the two limiting cases (short and long times), represented by eqs 5 and 6.  $D_0$ ,  $S/V$ , and  $\alpha$  are given in Table 2;  $S/V$  is indicative of the dimensions of the domains in which the  $\text{N}(\text{CH}_3)_4^+$  ion is able to move. Of course, the reality should be more complex and the transition between the two regions (very short and long diffusion intervals) should not be so abrupt. The quality of the actual experimental results did not, however, allow us to refine this analysis.

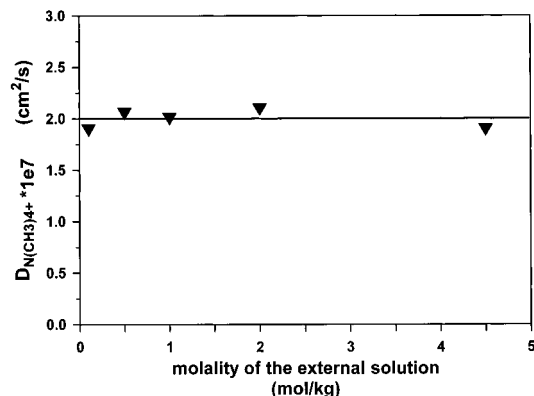
**TABLE 1: Measured Self-Diffusion Coefficients of  $\text{N}(\text{CH}_3)_4^+$  Ion in  $\text{D}_2\text{O}$  at Different Concentrations and of the Same Species Inside a Nafion Membrane Given in That Case as a Function of the Diffusion Interval  $\Delta$**

molality of $\text{N}(\text{CH}_3)_4\text{Cl}$ (mol/kg)	$\Delta$ (s)	$D_{\text{membrane}}$ ( $10^{-6} \text{ cm}^2 \text{ s}^{-1}$ )	$D_{\text{solution}}$ ( $10^{-6} \text{ cm}^2 \text{ s}^{-1}$ )
0.1			10.2
	0.3	0.12	
	0.4	0.108	
	0.5	0.10	
	0.6	0.096	
	0.7	0.096	
	0.8	0.086	
0.5			8.9
	0.3	0.121	
	0.4	0.109	
	0.6	0.097	
	0.7	0.096	
	0.8	0.087	
	0.9	0.086	
	1	0.087	
1			7.6
	0.3	0.101	
	0.4	0.10	
	0.6	0.096	
	0.7	0.095	
	0.8	0.094	
	1	0.093	
2			6.2
	0.4	0.102	
	0.6	0.095	
	0.8	0.091	
	1	0.094	

**TABLE 2: Values of the Self-Diffusion Coefficient of  $\text{N}(\text{CH}_3)_4^+$  Extrapolated at  $\Delta = 0$  ( $D_0$ ) inside a Nafion Membrane as a Function of the Molality of the External Solution**

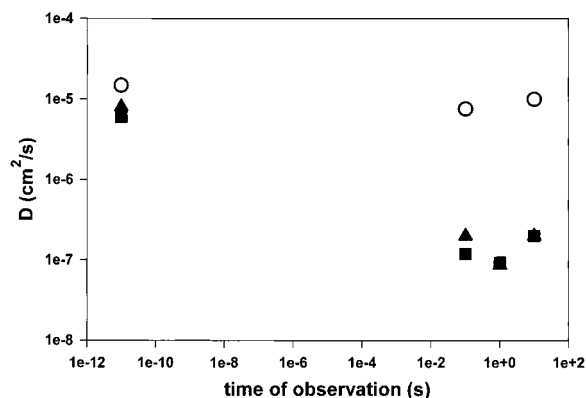
molality of $\text{N}(\text{CH}_3)_4\text{Cl}$ (mol/kg)	$D_0$ ( $10^{-6} \text{ cm}^2 \text{ s}^{-1}$ )	$S/V^a$ ( $\mu\text{m}^{-1}$ )	$\alpha^a$
0.1	0.20	0.65	2.3
0.5	0.20	0.65	2.3
1	0.115	0.26	1.2
2	0.12	0.32	1.3

<sup>a</sup>  $S/V$  and  $\alpha$  are parameters characterizing the porous medium (see text).



**Figure 8.** Variation of the self-diffusion coefficient of  $\text{N}(\text{CH}_3)_4^+$  in Nafion obtained by the radiotracer method versus the molality of external  $\text{N}(\text{CH}_3)_4\text{Cl}$  solution.

**3.3. Radiotracers.** here, one follows the transfer of  $\text{N}(\text{CH}_3)_4^+$  ions through the whole membrane. On Figure 8 are represented the values of the self-diffusion coefficient as a function of the molality of the external solution. No variation is noticed. This result is completely different from those obtained with smaller ions such as  $\text{Na}^+$  or  $\text{Cs}^+$  for which a clear dependence was



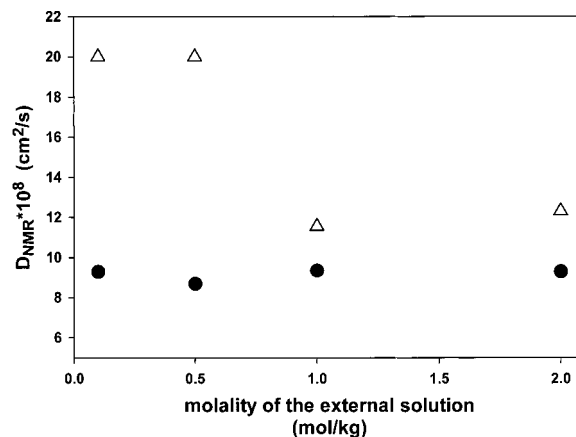
**Figure 9.** Self-diffusion coefficient of  $\text{N}(\text{CH}_3)_4^+$  in Nafion equilibrated with 0.5 mol/kg (▲) and 2 mol/kg (■)  $\text{N}(\text{CH}_3)_4\text{Cl}$  solution as a function of the times scale. For comparison the variation of the self-diffusion of  $\text{N}(\text{CH}_3)_4^+$  in 1 mol/kg nonconfined solution (○) has been also plotted.

observed when the electrolyte concentration was changed.<sup>31</sup> This difference may be ascribed to the ion size.

#### 4. Discussion

The values for the self-diffusion coefficients of  $\text{N}(\text{CH}_3)_4^+$  ions in Nafion membrane obtained from the different techniques, have been plotted as a function of the corresponding observation time scale in Figure 9. For comparison, the values of the self-diffusion coefficients of  $\text{N}(\text{CH}_3)_4^+$  ions in a 1 mol/kg  $\text{N}(\text{CH}_3)_4\text{Cl}$  solution have been also plotted. All the values for Nafion correspond to a process diffusion in the direction perpendicular to membrane plane, except for NQES experiments where the observed diffusion process is isotropic. In the latter case, there is no repercussion on analysis as the mean displacement observed by this technique is small compared to Nafion cavity size.

The NQES experiments allow one to study the self-diffusion process in Nafion cavities during some tens of picoseconds, which corresponds to a displacement over some angstroms. At this time scale, the process seems to be governed by solute–solvent collisions as it occurs in nonconfined solution. Some studies<sup>39–41</sup> have suggested the existence of pendent polymer chains in the hydrophilic domains. For this case, the viscosity of the internal solution would be higher than that of a nonconfined solution (of equivalent electrolyte concentration), and then the self-diffusion would be lower. The results of NQES experiments seem to indicate that the interface between the hydrophobic and hydrophilic domains is sharp, without pendent polymer chains inside cavities. This conclusion is in agreement with SANS studies,<sup>42</sup> theoretical calculations,<sup>43</sup> and FT-IR studies.<sup>44</sup> Other interesting information that can be drawn from these NQES experiments is about the strength of the interaction between the  $\text{N}(\text{CH}_3)_4^+$  ions and the anionic groups  $-\text{SO}_3^-$ . The  $\text{N}(\text{CH}_3)_4^+$  ions are located close to the wall of the cavity,<sup>45</sup> but the interaction with the anionic groups  $-\text{SO}_3^-$  is not strong enough to slow the self-diffusion process, as it has been observed for cesium ions by a radiotracer method.<sup>31</sup> The self-diffusion coefficient of  $\text{N}(\text{CH}_3)_4^+$  ions in Nafion cavities decreases with increasing electrolyte concentration, which could be due to viscosity effects. The self-diffusion coefficients obtained from the NMR experiments are lower than those from NQES experiments. The value of  $D_0$  represents the diffusion in a homogeneous network of cavities and so contains the transfer through the pores that connect cavities. The comparison of  $D_0$  values with the value obtained from NQES experiments thus provides important information about the transfer through these



**Figure 10.** NMR extrapolated value  $D_0$  (Δ) of the self-diffusion coefficient of  $\text{N}(\text{CH}_3)_4^+$  in Nafion versus the molality of external  $\text{N}(\text{CH}_3)_4\text{Cl}$  solution. Example of Nafion membrane equilibrated with 0.5 mol/kg. NMR value  $D_{\text{NMR}}$  (●) for long time Δ of the self-diffusion coefficient of  $\text{N}(\text{CH}_3)_4^+$  in Nafion versus the molality of external  $\text{N}(\text{CH}_3)_4\text{Cl}$  solution at long diffusion time Δ.

pores. Two orders of magnitude (see Figure 9) separate the two sets of values ( $D_{\text{NQES}}$  and  $D_0$ ), as compared to a factor of 2 for nonconfined solution. In Nafion membrane, this difference suggests that the transfer of  $\text{N}(\text{CH}_3)_4^+$  ions through the pores slows down considerably the diffusion process. This can be understood if one reminds that the diameter of  $\text{N}(\text{CH}_3)_4^+$  ion is 4.2 Å and that of the pores<sup>26</sup> is about 10 Å. The value of  $D_0$  depends on  $\text{N}(\text{CH}_3)_4^+$  ion concentration (Figure 10), as for  $D_{\text{NQES}}$ , but not in the same manner. SANS studies have shown that the Nafion structure depends on electrolyte concentration.<sup>34</sup> In particular, a local reorganization of the cavities may occur, that is cavities can merge. Nevertheless, SANS can only examine the cavities but not the pores; our NMR results seem to show that pore structure is also modified by the variation of electrolyte concentration.

When the observation time Δ is increased from 0.1 to 1 s, another dependence of the self-diffusion coefficient is observed (Figure 7). The model of Mitra and al.<sup>37</sup> shows that it may be interpreted by a diffusion process in a confined medium. The size of the domains is quite large compared with Nafion cavity size (difference of 4 orders of magnitude). One may interpret the restricted volume for diffusion by the presence of a heterogeneity in the distribution of cavities (zones of high density of cavities and zones of low density). This conclusion is supported by two recent studies: ultra-small-angle X-ray scattering (USAXS) studies seem to show the existence of large-scale heterogeneities;<sup>42</sup> moreover, an atomic force microscopy (AFM) study<sup>46</sup> has shown that the Nafion is composed of very tortured zones that are rich in ionic cavities. For Δ above 1 s, the self-diffusion coefficient no longer depends on Δ. On Figure 10 this apparent self-diffusion coefficient is plotted against electrolyte concentration: surprisingly no dependence is found versus this quantity. This means that, according to eq 6,  $D_0$  and α compensate each other. This feature may be related to the structural changes mentioned to above.

With the radiotracer method, we find again that the self-diffusion coefficient does not depend on electrolyte concentration (Figure 8), which confirms the above-mentioned NMR results. Nevertheless, the values obtained with the radiotracer method are twice larger than the NMR values. Two reasons may explain this difference: first, the measurements using radiotracers have been done with  $\text{H}_2\text{O}$  as solvent while  $\text{D}_2\text{O}$  was used for NMR measurements (the isotopic effect is known to be about 20% in nonconfined solution and we have verified

that, here, this isotopic effect is on the same order); second, the physicochemical properties of this industrial membrane may vary from one set to another. Unfortunately, the NMR and radiotracer measurements were performed with two different sets. An important result is that the same behavior is observed using both techniques. Their comparison indicates that no limiting factor influences transport in Nafion membranes for time scales greater than 1 s.

## 5. Conclusion

The study of the self-diffusion of  $\text{N}(\text{CH}_3)_4^+$  ions in Nafion membrane have been done at different time scales: during some tens of picoseconds (NQES), over 0.1 to 1 s (NMR) and during 100 s (radiotracer method). It has been shown that (1) the diffusion process inside Nafion cavities is similar to that in nonconfined solution, (2) the determining limiting factor of the diffusion of  $\text{N}(\text{CH}_3)_4^+$  ions is the transfer through the pores which connect cavities, (3) the distribution of cavities is not homogeneous, and (4) beyond 1 s, the self-diffusion for  $\text{N}(\text{CH}_3)_4^+$  ions depends neither on electrolyte concentration nor on the observation time scale.

The comparison of the results obtained from several experimental techniques provides important information on the limiting factors which govern transport processes in confined media.

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