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Interaction of the perfluorinated polymer Nafion-H with water studied by proton broad-line NMR at 4 K and MAS NMR at room temperature

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Broad-line ^1H NMR at 4 K shows that, when Nafion-H interacts with water molecules at low concentrations, the only species formed is the hydronium ion. The chemical shift of the unsolvated hydronium ion in Nafion-H with 1 H_2O/SO_3^-, determined by ^1H MAS NMR at room temperature, is 10.4 ppm relative to external TMS.

Keywords: Nafion; acid sites; hydronium ions; MAS NMR

1. Introduction

Nafion is a perfluorinated ion-exchange polymer used in various applications [1–3]. Many physical studies suggest that there is ionic clustering in Nafion [4,5]. These ionic domains are probably spherical, inverted micellar structures surrounded by a fluorocarbon matrix and connected by short channels. The size of the clusters depends on the equivalent weight, the solvent, and the nature of the cation. The catalytic activity of Nafion-H in a wide variety of organic reactions shows that the ionomer behaves as a superacid solid catalyst [2,3]. On the basis of its catalytic activity the acidity of Nafion-H on the Hammett scale, H_0, is estimated to be ~ -11 [6]. Using acid–base indicators, Sondheimer et al. [7] found the acid strength of Nafion-H is comparable to that of CF_3SO_3H. These authors studied the equilibrium $R_FSO_3H \rightleftharpoons R_FSO_3^- + H^+_{aq}$, and found an equilibrium constant 2.2. by partitioning a known amount of *o*-nitroaniline between the bulk water solution and the Nafion beads. Ferry [8] measured the Hammett acidity function of Nafion films equilibrated with a series of nitroaniline dyes in HCl solutions. He found that Nafion is a more acidic than acid solution up to 4.5 M HCl solution. Proton NMR studies of water in Nafion [9,10] show the chemical shift and the linewidth depend on the water content. Bunce et al. [11] found a linear relationship between

the proton content, determined by the ^1H NMR chemical shift, and the water content determined by weight change, and deduced a quantitative method for measuring the water content of Nafion samples swollen in a deuterated solvent.

Low temperature (generally 4 K) broad-line ^1H NMR using water molecules as base has allowed the determination of the dissociation coefficient of solid OH groups by simulation of the spectra. This coefficient is used to define an acidity scale of solids [12]. A limited study of the interaction of Nafion-H with water ($1\ H_2O/SO_3^-$) indicates that Nafion-H is the most acidic Brønsted solid on our scale [12].

We now report a wider investigation of Nafion-H interacting with small amounts of water.

2. Experimental

The powder form of Nafion-H was provided by E.I. Du Pont De Nemours and Co., Inc. All acid sites were activated as described in the Aldrich technical information bulletin (No. AL-163). 15 g of the polymer is stirred in a 3 M HCl solution at about 353 K for 3 h. The slurry is decanted and fresh 3 M HCl solution is added. The treatment with hot 3 M HCl solution is repeated three times. The resin is filtered, washed with distilled water until the washings are neutral and dried overnight at 373 K. The equivalent weight (0.95 meq/g) of the polymer was determined by pH metric titration with 0.1 N NaOH solution in presence of NaCl.

About 0.6 g of sample in a glass ampoule were evacuated at room temperature to 10^{-2} Pa, then heated at a rate of 24 K h^{-1} up to 463 K and held at this temperature for 7 days. The samples were slightly off-white. Water vapour was introduced at a constant temperature of 300 K in several steps, at pressures much lower than saturation, the amount of water being determined gravimetrically. The sample was held at 373 K overnight to ensure homogeneous distribution of the adsorbed water molecules and then sealed in thin 5 mm o.d. NMR tubes.

^1H MAS NMR-experiments at room temperature were performed on a Bruker MSL-400 spectrometer with a home-made 5 mm probe. The rotation frequency was 3.5–4.5 kHz. Chemical shifts are expressed relative to liquid TMS as external reference using the usual conventions. The broad-line ^1H NMR spectra were recorded at 4 K on a home-made continuous wave 60 MHz spectrometer with phase detection and signal accumulation. The spectra are absorption derivatives. They are theoretically symmetrical with respect to the centre and, in practice, the two parts of each experimental spectrum are averaged; for this reason we show only half of each spectrum. In both cases, ^1H MAS and broad-line NMR, the weak residual signal of the probe is subtracted from the total signal.

The simulated broad-line ^1H NMR spectra correspond to the weighted sum of the oxyprotonated species involved and for which magnetic configurations are calculated [13–18]: (i) H_2O, an r-distant two-spin configuration; (ii) H_3O^+, a magnetic

configuration with three r-distant spins at the vertices of an equilateral triangle; (iii) $H_2O \cdots HO$ or distorted H_3O^+, a magnetic configuration with three spins at the vertices of an isosceles triangle, where r is the base and r', the equal sides; (iv) OH, a two-spin configuration on a pure Gaussian and/or a pure Lorentzian function. Each of the corresponding functions (except the Gaussian and the Lorentzian functions) is convoluted by a Gaussian which takes into account the interaction between the protons of the configuration and those belonging to neighbouring configurations and also those on the non-zero spin nuclei in the environment (^{19}F in the present case). When the effect of these non-zero spins is small, the parameter of each Gaussian is related to a distance X which is close to the shortest distance between a proton of the configuration considered and a proton outside it. The numerical base takes into account the total number of protons in the sample, which is equal to the number of hydroxyl groups plus twice the number of water molecules introduced. Since the number of independent parameters for each simulation is high, certain constraints are applied. We impose the condition that the water molecules introduced do not dissociate to produce additional OH groups. The distances r found must lie in the range corresponding to the various oxygen–proton species identified and for each configuration the value of X must be greater than (or at least equal to) that of r and r'.

3. Results

3.1. ^{1}H MAS NMR AT ROOM TEMPERATURE

Fig. 1 shows the spectra of Nafion-H samples treated under vacuum at 463 K for 7 days and loaded with different amounts of water. All the spectra present a single signal whose position and linewidth vary with the water content. The spinning sidebands are weak in all spectra. The chemical shift increases on going from 0 H_2O/SO_3^- to 0.51 H_2O/SO_3^-, then decreases continuously for higher hydration levels. The chemical shift of the non-loaded sample is 10.6 ppm and the linewidth at half-height is 480 Hz. For Nafion-H with 0.51 H_2O/SO_3^- (fig. 1b), there is a dramatic change in both the chemical shift (11.9 ppm) and the broadening (4000 Hz). When Nafion-H contains 1 H_2O/SO_3^- (fig. 1c), the chemical shift moves upfield to the value of 10.4 ppm and the linewidth is 460 Hz. The linewidth of the Lorentzian signal associated with the samples with 1.6 H_2O/SO_3^- (fig. 1d) and 2.1 H_2O/SO_3^- (fig. 1e) is reduced and identical (120 Hz), while the chemical shifts are 9.2 and 8.5 ppm, respectively.

3.2. ^{1}H BROAD-LINE NMR AT 4 K

The proton broad-line spectra at 4 K of Nafion-H with n H_2O/SO_3^- ($n = 0.51$, 1.0, and 2.1) are shown in fig. 2. Despite accumulation of a relatively large number

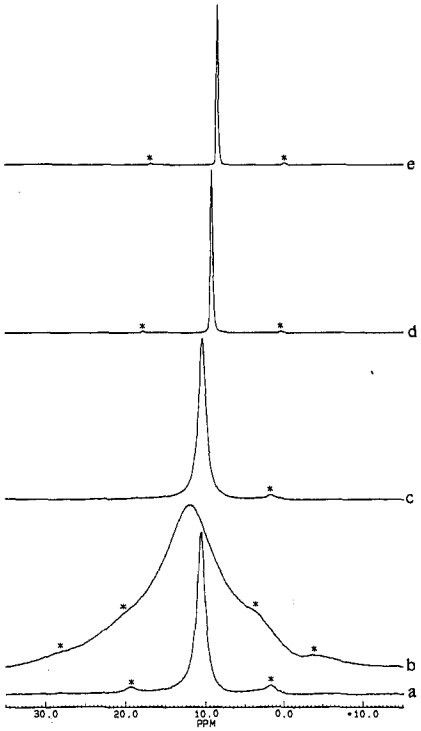

Fig. 1. ^{1}H MAS NMR spectra of Nafion-H samples treated at 463 K then loaded with the stated number of water molecules per SO_3^-: 0 (a); 0.51 (b); 1.0 (c); 1.57 (d); 2.1 (e). Asterisks denote spinning sidebands.

of scans (generally greater than 500) the signals are still noisy. The signal of hydronium ions is present in all spectra. For sample 0.51 H_2O/SO_3^- (fig. 2a), hydroxyl groups that are not interacting with water molecules are observed. Two Gaussian lines are necessary to represent these OH groups. The experimental spectrum of the sample 1.0 H_2O/SO_3^- is that of the hydronium ion species (fig. 2b). However, another simulation with a small number of OH groups is possible (fig. 2b′). In this case, all or almost all the acidic hydroxyl groups are interacting with water molecules. With 2.1 H_2O/SO_3^-, in addition of the signal of H_3O^+ ions, the line of water molecules is present. Table 1 summarizes the concentrations of the different oxyprotonated species for each sample and table 2 gives the distance parameters used to simulate the spectra.

4. Discussion

The chemical shift of the hydronium ion, $\delta_{H_3O^+}$, in Nafion-H with 1 H_2O/SO_3^- is 10.4 ppm, in good agreement with the result for Nafion-H swollen in

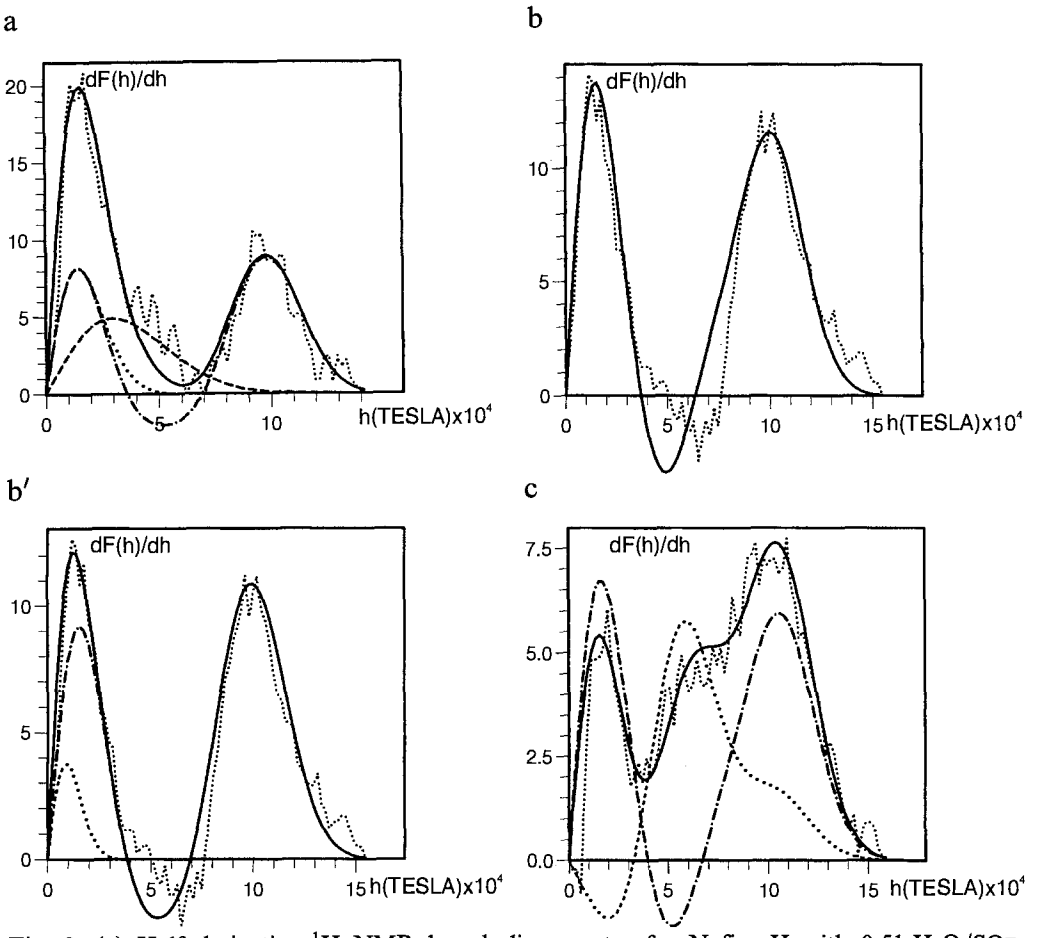

Fig. 2. (a) Half derivative ^1H NMR broad- line spectra for Nafion-H with 0.51 H_2O/SO_3^-. (···) Experimental, (——) fitted spectra, (- - -) weighted contribution of OH groups and (– · –) weighted contribution of H_3O^+ groups. (b) Half derivative ^1H NMR broad-line spectra for Nafion-H with 1.0 H_2O/SO_3^-. (···) Experimental and (——) fitted spectra = weighted contribution of H_3O^+ groups. (b′) Half derivative ^1H NMR broad-line spectra for Nafion-H with 1.0 H_2O/SO_3^-. (···) Experimental and (——) fitted spectra, (- - -) weighted contribution of OH groups and (– · –) weighted contribution of H_3O^+ groups. (c) Half derivative ^1H NMR broad-line spectra for Nafion-H with 2.1 H_2O/SO_3^-. (···) Experimental and (——) fitted spectra, (- - -) weighted contribution of H_2O groups and (– · –) weighted contribution of H_3O^+ groups.

cyclohexane-d_{12} [11]. $\delta_{H_3O^+}$ in deuterated alunite, deuterated superacid solutions and $H_3O^+ClO_4^-$ is 11.4 ppm, 10.3 ppm and 10.7 ppm, respectively [19–21].

The low sensitivity of the CW spectrometer combined with the low proton content of the resin explains why the 4 K ^1H NMR broad-line spectra are poor despite signal accumulation. We were unable to obtain an exploitable spectrum of the non-loaded Nafion-H samples. Such spectra could have yielded information about the H–H distances, the hydrogen bond strength and indicate whether water molecules are still present at any temperature. That there are no residual water mole-

Table 1
Number of oxygen-protonated species per SO_3^- after adsorption of the stated number of water molecules

No. of adsorbed water molecules per SO_3^-	No. of H_3O^+ ions per SO_3^-	No. of "free" acidic OH groups per SO_3^-	No. of water molecules per SO_3^-
0.0	0.0	1.00 ± 0.2	0.0
0.51 ± 0.05	0.51 ± 0.05	0.51 ± 0.05	0.0
1.00 ± 0.05	1.0 ± 0.2	0.0	0.0
	0.99 ± 0.20	0.04 ± 0.02	0.0
1.6 ± 0.1	1.04 ± 0.2	0.0	0.55 ± 0.05
2.1 ± 0.3	1.02 ± 0.2	0.0	1.07 ± 0.2

cules on dehydrated Nafion-H is shown by the fact that for 0.5 H_2O/SO_3^-, 0.5 OH groups are left for 1.0 H_2O/SO_3^-, only H_3O^+ ions are observed, as indicated in the following. In the case of Nafion-H all OH groups interacting with water molecules form H_3O^+ ions, unlike other solids, particularly zeolites, where some acidic OH groups are linked to water molecules by hydrogen bonds ($H_2O \cdots HO$ species). These results prove that Nafion-H is a very strong Brønsted acid. Simulation of the sample containing 0.51 H_2O/SO_3^- shows that 0.50 "free" acidic OH groups per SO_3^- are present, but the distribution of these hydroxyl groups not interacting with H_2O molecules is inhomogeneous. Two Gaussian lines are required to fit these species to the experimental spectrum. The H–H distance of 72% of these hydroxyl groups is 192 pm while 28% are 245 pm from each other. It is difficult to predict the structure of the acidic groups on dried Nafion-H from these observations since the presence of water molecules affects the hydrophilic domains [4,5]. The only species formed when $n = 1$ is the hydronium ion. The proton chemical shift, 10.4 ppm, in this case is that of this ion. An acceptable simulation of the proton broad-line spectrum is also obtained in the presence of a negligible amount (1.3% of the total number of protons) of OH groups left. This explains the choice of Nafion-H as the reference for the Brønsted acidity scale established by the 4 K

Table 2
Distances (in pm) used for simulations of Nafion-H·xH_2O spectra

No. of adsorbed water molecules per SO_3^-	Hydroxonium ions (isosceles symmetry)			Acidic OH groups		H_2O molecules	
	$r \pm 2$	$r \pm 5$	$X \pm 5$	$r \pm 2$	$X \pm 5$	$r \pm 2$	$X \pm 5$
0.51 ± 0.05	167		239 *	Gaussian	192		
				Gaussian	245		
1.00 ± 0.05	167	170	238				
	167		233 *	Gaussian	285		
2.1 ± 0.3	164	167	231			160	230

* Protons at the apices of an equilateral triangle.

broad-line proton NMR using water molecules as the base [12]. $\delta_{H_3O^+} = 10.4$ ppm is less than 11.9 ppm, the ^1H chemical shift of the sample containing 0.51 H_2O/SO_3^-. This is a priori surprising since $\delta_{H_3O^+}$ should be greater than $\delta_{OH} = 10.6$ ppm. This result proves that the shift of 10.6 ppm expresses not only the ionic character of these OH groups but also the influence of strong hydrogen bonds on the latter. IR studies on dried Nafion-H showed that the OH groups are involved in strong hydrogen bonds [5]. These hydrogen bonds between OH groups disappear after adsorption of water molecules. δ_{OH} should be lower than 10.6 ppm. Furthermore, $\delta_{H_3O^+}$ may be greater than 10.4 ppm in the 0.51 H_2O/SO_3^- sample because of hydrogen bonding. These bonds are broken in the 1 H_2O/SO_3^- sample. At the present state of our knowledge of the system we cannot be more precise. In the case of Nafion-H swollen in a solvent δ_H decreases continuously with increasing water content [11]. The fit of the spectrum of Nafion-H with 1 H_2O/SO_3^- obtained with the protons of H_3O^+ at the apices of an isosceles triangle (lowest symmetry ever programmed), gives 167 pm for the H–H distance of the base of the triangle and 170 pm for the side. The H–H distance for the protons at the vertices of an equilateral triangle is also 167 pm. Richards et al. found that H_3O^+ is pyramidal, with the H–H distance 172 pm in solid monohydrates of nitric, perchloric and sulfuric acids [22]. Neutron diffraction studies of hydronium ions in solids show that hydronium ions are hydrogen-bonded with neighbouring oxygen atoms [23,24]. These hydrogen bonds cause a slight distortion of the ions. The sample with 2 H_2O/SO_3^- shows "free" water molecules. The water molecules are those that contribute to the decrease in the chemical shift of the exchange signal. The environment of the hydronium ions is not significantly modified (the broadening distance parameter, X, has not significantly changed, see table 2). This suggests that the ions are not solvated at this water content.

5. Conclusion

Study of Nafion-H at low water contents using proton broad-line NMR at 4 K and high resolution NMR at room temperature has shown that Nafion-H is a very strong Brønsted acid. Complete ionization occurs when water interacts with the hydroxyl groups of the resin. The hydronium ions seem distorted by hydrogen bonding. The poor quality of the spectra makes it difficult to study the geometry of the ions. The chemical shift of the hydronium ions in Nafion-H with 1 H_2O/SO_3^- is 10.4 ppm.

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