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Proton NMR studies on concentrated aqueous sulfuric acid solutions and Nafion-H

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Sulfuric acid containing limited amounts of water, $H_2SO_4{\cdot}nH_2O$ with $0.23 \leqslant n \leqslant 4$, has been studied by ^1H broad-line NMR at 4 K and MAS NMR at room temperature. The broad-line NMR spectra indicate the formation of H_3O^+ and HSO_4^- ions. $H_2SO_4{\cdot}2H_2O$ is correctly written as $H_3O^+HSO_4^-{\cdot}H_2O$. The results are compared with the Nafion-H/water system.

Keywords: sulfuric acid, Nafion-H, acidity, hydronium ions, ^1H NMR

1. Introduction

H_2SO_4 and HF are catalysts widely used in industrial plants for the production of high-octane-number trimethylpentanes. The large amounts involved as well as the difficulties of handling, operating and regenerating these catalysts and the new regulations on the drastic reduction of aromatic compounds in gasoline encourage the development of heterogeneous superacidic catalysts [1]. Nafion-H, a Brønsted acid solid, with a small surface area, is known to catalyse various reactions such as the alkylation and transalkylation of aromatic hydrocabons and the dehydration of alcohols [2]. Although the unsupported polymer does not seem to be an effective alternative to liquid catalysts, a close comparison of the acid strength of H_2SO_4 and Nafion-H is undertaken in this paper by ^1H NMR techniques in order to emphasize the development of the supported resin for catalytic applications.

The acidity functions of aqueous solutions of sulfuric acid have been much studied [3,4]. Although differences are observed from one acidity function to another, they all show an increase in the acid strength of the system with increasing acid concentration. “Hydration” theory has been developed to explain these experimental observations [5]. The activity of all species is affected to some extent by solvation. The proton activity increases with decreasing water activity. The proton is less readily available from $H_3O^+(H_2O)_k$ (with $k \geqslant 1$) than from H_3O^+. At higher acid concentration, the proton is solvated by H_2SO_4, which is less basic than water. This weaker solvation explains the continuous rise in acidity. Calculations indicate that above 50 mol% H_2SO_4 the H_3O^+, $H_5O_2^+$, $H_7O_3^+$ and $H_9O_4^+$ species contribute to the acidity [6]. Experimental evidence for these species in various materials has been provided by X-ray crystallography and vibrational spectroscopy [7,8]. At lower acid concentration Robertson et al. [6] postulated the existence of $H_{21}O_{10}^+$. These authors consider that water clusters do not exist above 2 ± 1 M H_2SO_4.

Quantitative results from Raman spectra show that in dilute aqueous solutions nearly all the sulfuric acid is present as sulfate and H_3O^+ ions; at higher acid concentration most of it is in the form of HSO_4^- and H_3O^+ ions, and in very concentrated acid solutions (above 14 M) undissociated sulfuric acid prevails [9]. However, the presence of $H_5O_2^+$ in solutions above 14 M was suggested by Young et al. [10]. Using cryoscopic measurements, Gillespie [11] deduced the composition of 100% sulfuric acid. The major ionic components are HSO_4^- (0.0150 molal) and $H_3SO_4^+$ (0.01130 molal), which are responsible for the high conductivity of sulfuric acid. Different techniques showed that in highly concentrated aqueous solution the ionization of sulfuric acid is incomplete [9,12,13]. ^1H NMR experiments of sulfuric acid/water mixtures show a single line due to fast proton exchange between H_2O, H_2SO_4, H_3O^+ and HSO_4^- [14]. The dependence of the chemical shift on the water concentration is not linear from the pure acid to dilute aqueous acid solutions. The chemical shift increases from 100% H_2SO_4 up to around 17 M (about $H_2SO_4{\cdot}0.5H_2O$) then decreases at higher dilution. Richards and Smith [15,16] studied the structure of $H_2SO_4{\cdot}H_2O$ and $H_2SO_4{\cdot}2H_2O$ by ^1H NMR under rigid lattice conditions using the second moment method. They suggested the formula $H_3O^+HSO_4^-$ for the monohydrate, as also revealed by low-temperature X-ray data [17,18], but they could not distinguish between $H_3O^+HSO_4^-{\cdot}H_2O$ and $(H_3O^+)_2SO_4^{2-}$ for the dihydrate [16], while Taesler and Olovsson [19] determined by a three-dimensional single-crystal X-ray study at 83 K that the structure of $H_2SO_4{\cdot}2H_2O$ was $(H_3O^+)_2SO_4^{2-}$. Also using three-dimensional single-crystal X-ray data at 83 K, Kjällman et al. [20] showed that sulfuric acid tetrahydrate is in the form of $(H_5O_2^+)_2\,SO_4^{2-}$.

Nafion-H is a perfluorinated ion-exchange polymer with a predominantly polymeric hydrophobic backbone terminated by a highly acidic sulfonic acid group ($-SO_3H$) [21]. In solvents capable of removing the water chemically from within the beads, Nafion-H behaves as an acid of strength comparable to CF_3SO_3H, while the unsolvated Nafion-H·H_2O is comparable to concentrated sulfuric acid solutions containing over 95% H_2SO_4 [22].

We have already used proton broad-line NMR at 4 K and MAS NMR at room temperature to obtain quantitative and qualitative information about the environment of the protons interacting with water molecules in different Brønsted solids. An acidity scale for solids has been proposed on the basis of the ionization coefficient and the strength of the hydrogen bond of the $H_2O\cdots HO$ complex when ionization does not occur [23]. We now apply these techniques in the homogeneous phase for a better understanding of the acidity of concentrated sulfuric acid/water solutions. The lower limit of superacidity, arbitrarily proposed by Gillespie [24], being 100% H_2SO_4 for which $H_o = -12$, the results of the H_2SO_4/water mixtures are compared with those for the Nafion-H/water system.

2. Experimental

Reagent grade, 95–98% H_2SO_4 from Prolabo was used. Proton broad-line NMR at 4 K gave $H_2SO_4{\cdot}0.23H_2O$ for this concentrated acid solution, that is ca. 96% H_2SO_4, in agreement with the range of concentration given above. Acid solutions $H_2SO_4{\cdot}nH_2O$ with $n = 0.5, 1.0, 2.0, 3.0$ and 4.0 were prepared by dilution of the original reagent with distilled water and sealed in NMR tubes.

The powder form of Nafion-H was provided by E.I. Du Pont De Nemours & Co., Inc. All acid sites were activated by treatment with hot 3 M HCl solution. The equivalent weight (0.95 meq/g) of the polymer was determined by pHmetric titration against 0.1 N NaOH solution in the presence of NaCl. About 0.6 g of the sample in a glass ampule 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 samples were held at 373 K overnight to ensure homogeneous distribution of the adsorbed water molecules and then sealed in 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 of sealed tubes was 3.5–4.5 kHz. For sulfuric acid solutions MAS was not needed. Chemical shifts are expressed relative to liquid TMS as external reference using the usual conventions.

For MAS experiments, the samples were quenched in liquid helium, and the broad-line ^1H NMR spectra recorded at 4 K on a home-made continuous wave 60 MHz spectrometer with phase detection and signal accumulation. Proton MAS at 298 K and broad-line at 4 K NMR studies in heterogeneous systems showed that during quenching the equilibrium is not significantly modified [25]. 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 for the Nafion-H/water system and neglected for the acid solutions.

3. Data analysis of ^1H broad-line NMR

The simulated broad-line ^1H NMR spectra correspond to the weighted sum of the oxyprotonated species involved and for which magnetic configurations are calculated [26–31]: (i) H_2O, a $\boldsymbol{r}$-distant two-spin configuration [26]; (ii) H_3O^+, a magnetic configuration with three $\boldsymbol{r}$-distant spins at the vertices of an equilateral triangle [27,28]; (iii) $H_2O\cdots HO$ or distorted H_3O^+, a magnetic configuration with three spins at the vertices of an isosceles triangle, where $\boldsymbol{r}$ is the base and $\boldsymbol{r}'$ the equal sides [29,30]; (iv) OH, a two-spin configuration or a pure Gaussian and/or a pure Lorentzian function [31]. 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 of the non-zero nuclei spin in the environment (^{19}F in the case of Nafion-H). When the effect of these non-zero spins is small the parameter of each Gaussian is related to a distance $\boldsymbol{X}$ which is close to the shortest distance between a proton of the configuration considered and a proton outside it.

Each experimental spectrum generally presents three maxima representative to a first approximation of the oxyprotonated chemical species formed in the sample:

– at about 1×10^{-4} Tesla due to "free" OH groups and/or interaction with water molecules and/or participating in the formation of the hydronium ion,

– at about 6×10^{-4} Tesla due to "free" water molecules and/or to the hydrogen-bonded species,

– at about 10×10^{-4} Tesla due essentially to the hydronium ion.

The usual procedure for simulating the NMR broad-line spectra is as follows. During the first attempts, we associate a priori the highest number possible of protons of water molecule and OH groups into three-spin isosceles magnetic configurations for the following reasons.

If the chemical bond and/or the hydrogen bond between these groups really exists, we find a correct chemical balance, i.e. conservation of the total number of OH groups and of the number of adsorbed water molecules. It will not be the case if we suppose these species primarily magnetically independent [29].

If water molecules and the OH groups do not form hydrogen bonds, two situations can arise:

(i) Water molecules and OH groups are relatively "diluted". It is possible and even frequent that a good simulation of broad-line spectra is obtained with a correct chemical balance using the three-spin isosceles magnetic configurations. However, the $\boldsymbol{r}'$ value of the sides of the triangle is so high that it excludes the formation of the hydrogen bond. In such a case, the chemical composition is obtained by simulating the contributions of the OH groups and of water molecules separately [32].

(ii) Water molecules form "clusters". It is not possible to simulate the broad-line spectra of such populations by three-spin configurations of protons. The form of the calculated contributions to the spectra will not fit the experimental spectrum. Moreover, in the case of water molecules "clusters", the shortest distance between H atoms belonging to two distinct water molecules, $\boldsymbol{X}$, would inevitably be shorter than the values of $\boldsymbol{r}'$ to try for the three-spin isosceles configuration.

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. Since the number of independent parameters for each simulation is high certain constraints are applied. The distances $\boldsymbol{r}$ found must lie in the range corresponding to the various oxygen–proton species identified, and for each configuration the value of $\boldsymbol{X}$ must be greater than (or at least equal to) that of $\boldsymbol{r}$ and $\boldsymbol{r}'$.

4. Results

4.1. *Sulfuric acid solutions*

4.1.1. *^{1}H MAS NMR at room temperature*

The spectra of sulfuric acid solutions show a single Lorentzian signal whose chemical shift increases with the acid concentration from 8.7 ppm for $H_2SO_4{\cdot}4H_2O$ to 11.2 ppm for $H_2SO_4{\cdot}0.5H_2O$ and then decrease in agreement with refs. [13,14] (table 1). The line-width at half-height is about 160 Hz for all spectra.

4.1.2. *^{1}H broad-line NMR at 4 K*

The simulated broad-line spectra are shown in figure 1. The shape of the experimental spectrum is affected by increasing dilution. All spectra present a maxima at around 2×10^{-4} T and 10×10^{-4} T and a minimum at around $(6–7) \times 10^{-4}$ T except for the spectum of the sample $H_2SO_4{\cdot}4H_2O$ for which a minimum is observed at 3.5×10^{-4} T.

The simulation of the spectra shows the presence of hydronium ions and unreacted hydroxyl groups in all spectra. Two contributions are used to simulate the spectra of $H_2SO_4 \cdot nH_2O$ samples with $0.23 \leqslant n \leqslant 1$: the contribution of the hydronium ions and that of hydroxyl groups. The hydroxyl groups signal is not resolved to differentiate the OH groups from sulfuric acid and the HSO_4^- ions. For $n = 1$, the concentrations of H_3O^+ and of HSO_4^- ions are identical and equal to that of SO_4 groups. At higher values of n, in addition to the latter contributions, the signal of water molecules appears. Attempts to simulate water molecules and hydroxyl groups with a single signal in which protons of these two species are at the vertices of an isosceles magnetic configuration ($H_2O\cdots HO$) failed. The hydronium ions have the highest symmetry at any concentration. These ions are not distorted, since simulations with protons at the apices of an isosceles triangle were unsuccessful. The hydroxyl groups are fitted with Pake's two-spin model in which the intra-proton distances are greater than the H–H distance of water molecules (table 1). The H–H distance of the hydroxyl groups decreases with increasing

Table 1
Number of oxygen-protonated species per H_2SO_4 after adsorption of the stated number of water molecules, distances (in pm) used for simulations of the spectra and chemical shift relative to external TMS

No. of adsorbed water molecules per $H_2SO_4 \pm 3\%$	Hydronium ions (equilateral symmetry)			Acidic OH groups			H_2O molecules			$\delta_{^1H}$ ±0.1 (ppm)
	No.±10%	$r \pm 2$	$X \pm 5$	No.±10%	$r \pm 5$	$X \pm 5$	No.±10%	$r \pm 2$	$X \pm 5$	
0.23	0.23	166	267	1.77	238	291	0.0			11.1
0.50	0.50	167	265	1.50	236	270	0.0			11.2
1.00	0.96	167	255	1.04	225	285	0.0			10.9
2.0	1.00	167	253	1.00	217	269	0.92	147	198	10.1
3.0	1.05	166	248	0.95	204	243	1.75	152	198	9.2
4.0	1.00	165	247	1.0	202	241	3.00	151	196	8.7

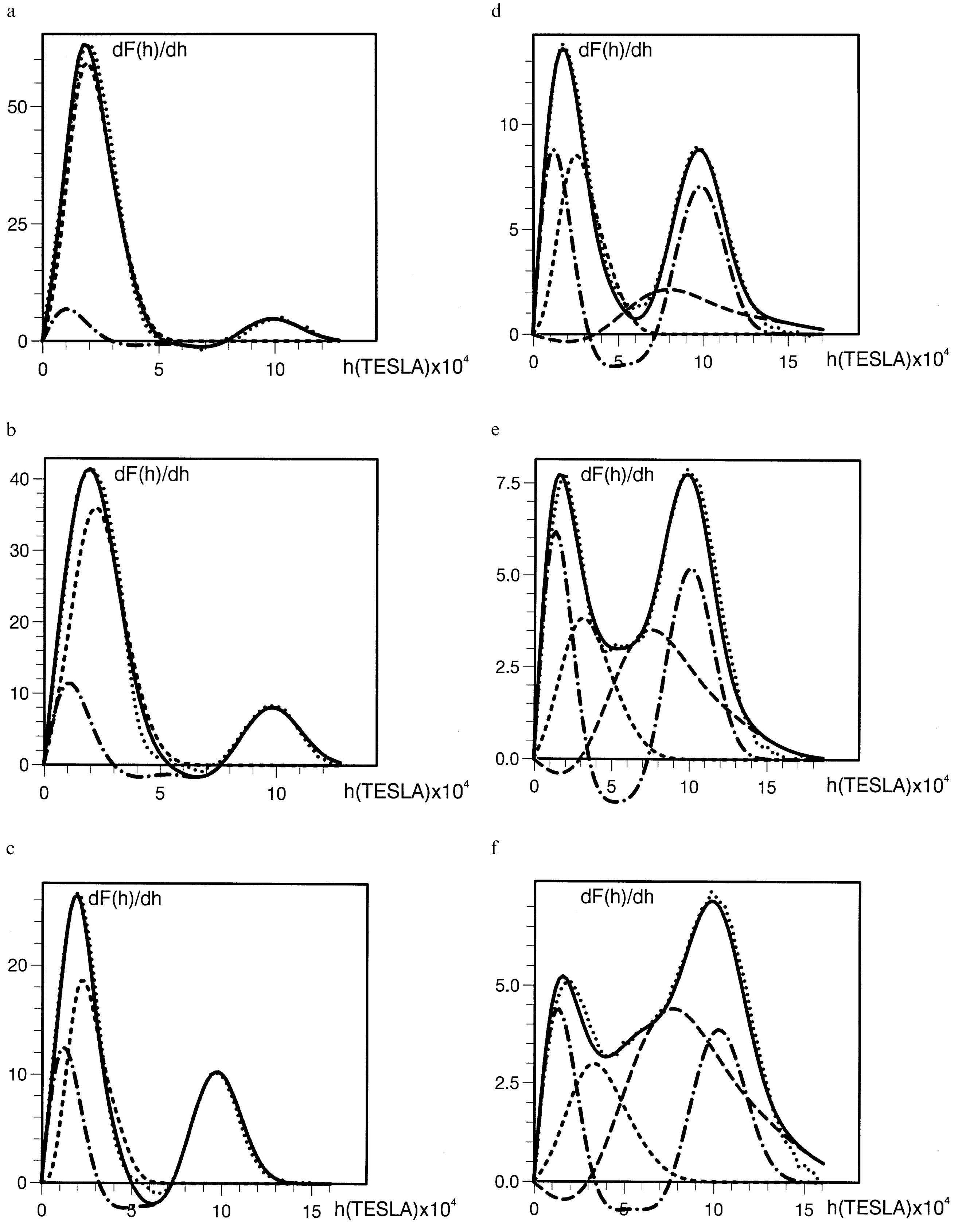

Figure 1. Half derivative ^{1}H NMR broad-line spectra of $H_2SO_4 \cdot nH_2O$. (a) $n = 0.23$, (b) $n = 0.5$, (c) $= 1.0$, (d) $n = 2.0$, (e) $n = 3.0$, (f) $n = 4.0$. (···) Experimental, (——) fitted spectra, (- - -) weighted contribution of OH groups, (-·-·-) weighted contribution of H_3O^+ groups and (– –) weighted contribution of water molecules. $dF(h)/dh$ in a.u. is the derivative of the absorption signal, $F(h)$, where h is the variation of the applied magnetic field relative to the centre of the spectrum.

dilution. Table 1 summarizes the concentrations of the different oxyprotonated species for each sample and the distance parameters used to simulate the spectra.

4.2. Nafion-H/water system

It should be remembered that Nafion-H contains a single H acid per SO_3^- group. We will briefly summarize the results obtained with this system. The details are given in ref. [33].

4.2.1. ^{1}H MAS NMR at room temperature

All the spectra present a single signal whose position and line-width vary with the water content. The chemical shift increases, going from 10.6 ppm for zero H_2O/SO_3^- (line-width at half-height 480 Hz), through a maximum at 11.9 ppm for ca. 0.5 H_2O/SO_3^- (line-width 4000 Hz), and then decreases continuously for higher hydration levels to 8.5 ppm for 2.1 H_2O/SO_3^- (line-width 120 Hz). The chemical shift of Nafion-H containing 1.0 H_2O/SO_3^- is 10.4 ppm (table 2).

4.2.2. ^{1}H broad-line NMR at 4 K

Despite signal accumulation, the broad-line spectra are still noisy because of the low proton content of Nafion-H and the low sensitivity of the spectrometer. Under such conditions the spectrum of the unloaded sample of Nafion-H could not be used. All spectra of hydrated Nafion-H samples contain hydronium ions. For the sample with 0.51 H_2O/SO_3^-, hydroxyl groups not interacting with water molecules are observed. Two Gaussian lines are necessary to represent these OH groups. The experimental spectrum of the sample with 1.0 H_2O/SO_3^- is simply that of the hydronium ion species. In this case, all the acidic hydroxyl groups are interacting with water molecules. For x H_2O/SO_3^- with $x \geqslant 1$, the symmetry of the hydronium ions is no longer maximal; the ions are slightly distorted and better represented by an isosceles triangle. With 2.1 H_2O/SO_3^-, in addition to the signal of H_3O^+ ions, the signal for water molecules is present. The distance between neigbouring proton configurations decreases but not significantly with increasing dilution. Table 2 summarizes the concentrations of the different oxyprotonated species for each sample and the distance parameters used to simulate the spectra.

5. Discussion

We shall first discuss the strength of the two Brønsted acid sites of sulfuric acid. Then, we shall compare the geometry of the hydronium ions in the H_2SO_4/water and Nafion-H/water systems. Finally, the chemical shift of the hydronium ions in $H_3O^+HSO_4^-$ is deduced from the study of similar systems.

Proton NMR spectra at 4 K of samples of $H_2SO_4{\cdot}nH_2O$ when $n \leqslant 1$, clearly show that the reaction: $H_2SO_4 + H_2O \longrightarrow H_3O^+ + HSO_4^-$ is complete. For $H_2SO_4{\cdot}nH_2O$ with $n \geqslant 1$, in addition to water molecules and hydronium ions, there are still hydroxyl groups in an amount equivalent to one OH/SO_4. The failure to group H_2O and OH in a single three-spin magnetic configuration proves that there is no interaction between water molecules and the hydroxyl groups. Water molecules are arranged in clusters, as we shall see later. This also indicates that only one of the two acidities of H_2SO_4 is strong, in agreement with the literature. This first acidity yields hydronium ions. The interaction under study involves H_2SO_4, H_3O^+, HSO_4^- and H_2O, depending on the number of water molecules present.

Simulation of the spectra indicates an equilateral symmetry for H_3O^+ ions in the H_2SO_4/water system, in agreement with low temperature X-ray data [17,18]. The distance between the hydrogen atoms is 165–167 ± 2 pm. This distance is almost constant from $H_2SO_4{\cdot}0.23H_2O$ to $H_2SO_4{\cdot}4.0H_2O$. The structure of the hydronium ions is not significantly disturbed by hydration. Richards and Smith [15] found 172 ± 2 pm for the monohydrates of nitric and perchloric acids using the second moment of

Table 2

Number of oxygen-protonated species per SO_3^- after adsorption of the stated number of water molecules, distances (in pm) used for simulations of the spectra of the Nafion-H/water samples and chemical shift relative to external TMS

No. of adsorbed water molecules per SO_3^-	Hydronium ions (isosceles symmetry)				Acidic OH groups [a] No. per SO_3^- ± 10%		H_2O molecules			$\delta_{^1H}$ ±0.1 (ppm)
	No. per SO_3^- ± 10%	$r \pm 2$	$r' \pm 2$	$X \pm 5$			No. per SO_3^- ± 10%	$r \pm 2$	$X \pm 5$	
0.0	0.0				1.00		0.0			10.6
0.51 ± 0.05	0.51		167	239 [b]	0.37	G 192	0.0			11.9
					0.14	G 245				
1.00 ± 0.05	1.02	167	170	238	0.0		0.0			10.4
	0.99	167		233 [b]	0.04	G 285	0.0			
1.6 ± 0.1	1.04	167	170	232	0.0		0.55	161	245	9.2
2.1 ± 0.3	1.02	164	167	231	0.0		1.07	160	230	8.5

[a] G Gaussian line.

[b] Protons at the apices of an equilateral triangle.

spectra recorded at 90 K, and they assumed the same value for sulfuric acid monohydrate. The spectrum of sulfuric acid dihydrate by this method was too complex for the authors to reach any conclusion [16]. In contrast to the analytical method used here to simulate our broad-line NMR spectra, the second moment method gives an average distance over a wide range of values. Our results at 4 K show that the formula of sulfuric acid dihydrate is H_3O^+ $HSO_4^-\cdot H_2O$.

The oxygen-protonated species distances are given in table 1. From this table we have an insight into the interaction of hydronium ions with their environment. The nuclear spin of the oxygen-16 and sulfur-32 atoms is zero. The abundance of other isotopes is negligible. Consequently, the X-values of the different magnetic configurations are directly related to the average inter-proton distances. The distance between hydronium ions and neighbouring protons decreases with increasing dilution (table 1).

In the Nafion-H/water system, the hydronium ions in the sample with 0.5 H_2O/SO_3^- have an equilateral symmetry with an internal distance of 167 ± 2 pm. This value is comparable to the internal distance of hydronium ions in the sulfuric acid/water system. At higher value of H_2O/SO_3^-, the hydronium ions are slightly distorted and represented by an isosceles triangle (table 2). The base of the triangle is 164–167 ± 2 pm and the side 167–170 ± 2 pm. The internal distances decrease slightly with dilution. In this system also the X-values decrease with increasing dilution. These values are shorter than in sulfuric acid/water mixtures. These results suggest that the hydronium ions are in stronger interaction with their environment in Nafion-H/water than in the sulfuric acid/water system.

To understand the organization of the oxyprotonated species in these systems, the concentration and the distance parameters of all magnetic configurations should be studied. We could not obtain the broad-line spectrum of the unloaded Nafion-H for the reasons already given in the Results section: low proton content of the sample and low sensitivity of the spectrometer.

In the sample containing 0.5 H_2O/SO_3^- two Gaussian lines are used to represent the unreacted hydroxyl groups. The H–H distances in these two sets of OH groups are very different. This suggests that the distribution of these groups is not homogeneous. 0.37 OH/SO_3^- groups of the unreacted hydroxyl groups are 192 ± 5 pm from other protons. Nearby fluorine atoms probably influence these hydroxyl groups since a distance of 192 pm is not usual for a set of OH groups interacting with each other. The distribution of the hydroxyl groups observed may also be due to hydroxyl groups located at different positions in Nafion-H. Gierke and Hsu [34] proposed a model for ionic clustering in Nafion-H, in which the polymeric ions and absorbed phase separate from the fluorocarbon backbone into approximately spherical clusters connected by short narrow channels. These channels also contain OH groups. Gierke et al. [35] found that the size of the spherical clusters and the channels decrease with decreasing water content of the polymer. The cluster in dried 1200-equivalent-weight polymer is about 1900 pm in diameter and contains ca. 26 ion-exchange sites.

All Nafion-H OH groups interact with water in the sample with 1.0 H_2O/SO_3^- to yield only hydronium ions. Relative to water, the acid strength of Nafion-H is identical to the first acidity of sulfuric acid. This levelling effect of water is observed on strong acids. In the Nafion-H sample with 1.0 H_2O/SO_3^-, the inter-proton distance of the hydronium ions is about 238 pm. The influence of more water molecules on this distance is observed on the sample containing 2.1 H_2O/SO_3^-. The distance between H_3O^+ and H_2O species remains almost constant (230 pm in Nafion-H with 2.1 H_2O/SO_3^-). The interaction between species is not significantly modified at these dilution levels.

In summary, in the Nafion-H sample containing 0.5 H_2O/SO_3^-, "free" OH groups and H_3O^+ coexist. In the sample with 1.0 H_2O/SO_3^-, the sole species is H_3O^+, 238 pm apart. With 2.1 H_2O/SO_3^-, H_3O^+ and H_2O coexist. They are separated by 230 pm.

In the case of sulfuric acid/water mixtures more species are involved. However, as already mentioned, there is no interaction between OH groups and water molecules in the $H_2SO_4\cdot nH_2O$ samples with $n \geqslant 1$. The simulation with the protons at the apices of an isosceles triangle was unsuccessful. This supports the fact that water molecules are organized in small "clusters". Moreover, the H–H distance between these water molecules is 196–198 ± 5 pm, very different from the inter-proton distances of the other two species (241–291 ± 5 pm). This also supports the idea of water molecule aggregates. Refering to the second moment method, Yaroslavtsev et al. [36] estimate that water aggregates are formed for solutions containing more than four water molecules per acid proton. Our results also show that the hydronium ions are close to HSO_4^- ions, since the X-values of these species are comparable but very different from those of water molecules (table 1). In this case, the inter-proton interactions increase significantly with hydration. Let us recall that to explain the acid strength of sulfuric acid solutions the "hydration" theory was suggested (see Introduction) in which the activity of the proton is related to the degree of dilution of sulfuric acid. The Hammett acidity function, H_o, of the solutions of composition $H_2SO_4\cdot 2H_2O$, $H_2SO_4\cdot 3H_2O$ and $H_2SO_4\cdot 4H_2O$ is −6.05, −4.97 and −4.08, respectively [37]. As described above, the environment of most species is somewhat affected by the increasing inter-proton interactions. We cannot relate our results to the "hydration" theory to explain the acid strength of the above solutions. However, as already pointed out, the parameter X is well defined for one type of inter-proton magnetic configuration when the effect of the non-zero spins present in the system is small. Being an average value, **X** may not precisely represent the true distribution of protons in a complex set of different magnetic configurations. This should be the case of the sample of $H_2SO_4 \cdot nH_2O$ with $n \geqslant 2$. Moreover, weak hydrogen bonds cannot be detected by this method.

The proton chemical shifts, $\delta_{^1H}$, (8–12 ppm) observed in Nafion-H/water and H_2SO_4/water samples are characteristic of strong acids or strong hydrogen bonds [14,38–41]. We did not study 100% H_2SO_4. However, according to the literature [14], for pure sulfuric acid $\delta_{^1H} = 10.8$ ppm relative to TMS. In both systems under study, the dependence of $\delta_{^1H}$ on the water concentration is the same. $\delta_{^1H}$ increases from low water concentrations to a maximum at around $H_2SO_4 \cdot 0.5H_2O$ (11.2 ppm) for sulfuric acid and 0.5 H_2O/SO_3^- (11.9 ppm) for Nafion-H. Previous ^1H NMR studies on sulfuric acid have already revealed this variation [13]. The maximum chemical shift is observed when about half the strong acid sites have reacted with water to form hydronium ions. At this concentration, in addition to the electrostatic interactions arising from the formation of the ions, strong hydrogen bonds still exist [18]. Both effects have a considerable impact on the chemical shift. The chemical shift of the hydronium ions, $\delta_{^1H} = 10.4$ ppm, in Nafion-H containing 1.0 H_2O/SO_3^- is unambiguously defined, since H_3O^+ ions are the sole protic species. In $H_2SO_4 \cdot H_2O$, $\delta_{^1H} = 10.9$ ppm; only two oxygen-protonated species are present: H_3O^+ and HSO_4^-. The interactions (proton exchange, electrostatic and hydrogen bonds) between these species affect the chemical shift, so we cannot readily determine the individual contributions of each species to the mean chemical shift. Ratcliffe et al. reported $\delta_{^1H} = 11.7$ ppm for HSO_4^- in NH_4HSO_4 [38], while Gillespie et al. [42] deduced $\delta_{^1H} = 13.9$ ppm (relative to pure water, ca. 18.7 ppm on our scale) for HSO_4^- from the study of metal hydrogen sulfate solutions in sulfuric acid, and Mastikhin et al. [43] gave $\delta_{^1H} = 13.5$ ppm for HSO_4^- in $KHSO_4$. These values demonstrate the influence of hydrogen bonds on the chemical shift. Using the values of 11.7 and 13.5 ppm and the data in table 1 for the number of H_3O^+ and HSO_4^-, we find $\delta_{^1H} = 10.9$ and 10.3 ppm, respectively, for H_3O^+ in $H_3O^+HSO_4^-$. These values are comparable to the value of 10.4 ppm for H_3O^+ in Nafion-H 1.0 H_2O/SO_3^- sample. Gillespie et al. estimated a shift of 5.2 ppm (relative to pure water, ca. 10 ppm on our scale) for H_3O^+ in excess sulfuric acid [42].

6. Conclusion

The simulation of the proton broad-line NMR spectra of concentrated aqueous solutions of sulfuric acid of compositions $H_2SO_4 \cdot nH_2O$ with $0.23 \leqslant n \leqslant 4$, recorded at 4 K, shows that the reaction between the acid and water molecules is complete for the first acidity of H_2SO_4. The first acidity of sulfuric acid is strong, yielding hydronium ions in the same way as the hydroxyl groups of Nafion-H. The results suggest that water molecules form small clusters in $H_2SO_4 \cdot nH_2O$ with $n \geqslant 1$. The interactions between species increase with dilution. The slight changes observed in the internal and external distances of the species may cause changes in their activity and be responsible for the decrease in the acid strength with dilution in the range of concentrations studied. The formula of sulfuric acid dihydrate is $H_3O^+HSO_4^- \cdot H_2O$. The chemical shift of the hydronium ions in $H_3O^+HSO_4^-$ cannot be estimated directly, as in Nafion-H·1H_2O where H_3O^+ is the only species ($\delta_{^1H} = 10.4$ ppm). We deduce that the proton chemical shift of the hydronium ions in $H_3O^+HSO_4^-$ is around 10.3–10.9 ppm. Water proves to be too strong a base to be able to differentiate sulfuric acid and Nafion-H. Studies with weaker bases are being undertaken.

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