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Proton NMR Method for the Quantitative Determination of the Water Content of the Polymeric Fluorosulfonic Acid Nafion-H

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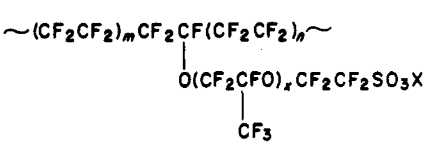
ABSTRACT: Conditions have been worked out for determining the absolute water content of Nafion-H by proton NMR. The relative areas of the resonances due to hydroxylic protons can be compared directly with those due to a proton reference substance added in known amount, provided that proper precautions are taken to detect the protons of the sample and those of the reference with equal sensitivity. A linear relationship is obtained between the proton content determined by NMR and the water content determined by weight changes. In certain swelling solvents, the chemical shift of the hydroxyl resonance is strongly dependent on the water content, and the chemical shift alone may be used as an indirect measure of the water content. Nafion-H dried in vacuo to constant weight at room temperature is the monohydrate, i.e., $R_FSO_3^-\cdot H_3O^+$.

Introduction

Nafion-H is the name commonly used for the acidic form of a series of perfluorinated polymeric sulfonic acids 1 manufactured by E. I. du Pont de Nemours Co., Inc. The salts (1, X = metal ion) find many uses as ion exchangers and as membrane separators in various electrochemical applications, while the free acid (1, X = H) has been found to be a very effective acidic catalyst for a wide variety of organic chemical reactions.[1]



$$\sim(CF_2CF_2)_mCF_2CF(CF_2CF_2)_n\sim \quad \text{with } O(CF_2CF(CF_3)O)_xCF_2CF_2SO_3X \text{ on } CF$$

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Although these perfluorosulfonic acids are not covalently cross-linked, they nevertheless have considerable internal structure. This structure has been the subject of many previous investigations and is the reason for the ion transport properties of the polymer. All models for the structure of the polymer presuppose more than one phase, a fluorocarbon-like phase and at least one aqueous phase that to some degree solvates the sulfonate anion groups of the salts (or the sulfonic acid groups of the free acid).

The catalytic activity of Nafion-H, the acidic form of the polymer, depends critically on the water content, yet there has so far been no analytical method for determining the water content of Nafion absolutely. Titration methods suffer from lack of precision since the equivalent weight of the polymer is so great. Infrared analysis has been used recently,[2] but the complexity of the O–H stretching region of the spectrum makes quantitative interpretation difficult.

Previous authors have taken various arbitrary "standard states" of Nafion-H as the benchmarks for their structural and analytical studies. These include Nafion dried to constant weight at 170 °C,[3] dried at 160 °C,[4] dried for 30 min at 220 °C under 10^{-4}-torr pressure,[5] and dried at 100 °C for 18 h in vacuo.[6] The absolute water contents of these structures are unknown, as is their relationship to each other.

The object of the present work was to develop a quantitative method of measuring the absolute water content of Nafion-H by proton NMR spectroscopy. This has been achieved, and we have also been able to identify the chemical species that are present after drying the polymer under specified conditions. In addition, we have succeeded in calibrating a method for determining the water content of Nafion-H by measuring the chemical shift of the hydroxylic protons in a simple standard procedure.

Results and Discussion

A. Choice of a Reference State. The reference state adopted throughout this work was Nafion-H that had been dried in vacuo to constant weight at room temperature. This material was later shown to have constant water composition (section D) and could be obtained reproducibly at different levels of vacuum. Constant weight was achieved in as little as 10 h (~10^{-5} torr) or as long as 340 h (~1 torr). Bench-dried Nafion-H was not satisfactory as a reference state because its water content varied with the humidity. For example, the weight loss (assumed to be exclusively water: for justification, see ref 5) from the bench-dried material to the reference state varied from 3.2% in winter to 6.2% on a particularly humid summer day. More typical weight losses were 4–5%.

Rehydration from the above reference state was relatively slow, and samples could be handled without special precautions in the air. When samples had to be stored for more than a few minutes, however, they were kept in sealed glass ampules to guard against atmospheric rehydration.

B. Qualitative NMR Experiments. The proton NMR spectra of Nafion-H samples swollen in water show two resonances: one, 4.8 ppm downfield from external Me_4Si, appears at the frequency of pure water, and the other appears further downfield. A similar phenomenon has been reported for poly(styrenesulfonic acid), which exhibits two hydroxylic proton resonances upon swelling in water or methanol.[7,8] The upfield OH resonance is ascribed to water that is external to the polymer beads, and the downfield one to "internal" water, which is solvating the SO_3H groups. The downfield shift of this resonance is analogous to that of the hydroxyl resonance in aqueous solutions of mineral acids.[9]

A sample of Nafion-H containing 12% water relative to the reference state was placed in sufficient D_2O to swell the polymer, and the ^1H NMR spectrum was recorded. The "internal" and "external" OH resonances were of comparable areas, and their ratio did not change over several hours. This experiment indicates that the diffusion of water in and out of the Nafion beads is faster than the time needed to prepare the sample, although the observation of two resonances indicates that it is slow "on the NMR time scale".

Spectral changes were observed when this same sample was kept for longer periods. After 30 h, the downfield (internal) OH resonance had increased in relative area by a small proportion (~10%) and had shifted closer to the "external" water peak. This long-term change in the spectrum was attributed to conformational changes in the Nafion structure. The proportion of the aqueous phase

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Table I
Separation, $\Delta\delta$, in ppm of Internal and External OH Resonances in Nafion-H Swollen in Water (or D_2O)

treatment	$\Delta\delta$, ppm
(a) powder swollen in water	1.1
(b) sample (a) after 30 h	0.8
(c) powder pretreated by boiling in water	0.5
(d) powder pretreated with water at 170 °C, 4 h	0.3

increases, and the internal water resonance shifts upfield because the acidity of the aqueous phase is lower. In the terminology of the "cluster" model of Nafion structure,[10] the aqueous clusters increase in size.

The separation between the two OH resonances is reduced further if the Nafion samples are pretreated by heating in water, see Table I. These highly hydrated samples are discussed further in section D.

Internal and external hydroxylic resonances can also be seen if Nafion-H is swollen in methanol or in aqueous acetonitrile. For example, in mixtures of methanol and CCl_4, three resonances are observed: 3.3 (CH_3), 4.8 (external OH, not observed at low proportions of methanol, presumably because all the methanol is then internal), 5.9–8.6 ppm. This last resonance is assigned to the internal OH. As the internal acidity increases concurrent with decreasing proportion of CH_3OH in the solvent, this resonance shifts progressively downfield. The value 8.6 ppm is reached at 1% methanol by volume.

As in water, there is no change in the relative areas of the internal and external OH resonances in either CH_3OH or CH_3OD over several hours. Equilibration is complete by the time the polymer is swollen. Furthermore, no change in line shape is seen over the temperature range −55 to +70 °C. With $\Delta\delta = 1.1$ ppm ($\equiv$65 Hz at 60 MHz), the rate of exchange between internal and external OH is less than 65 Hz, even at 70 °C. This result at first seems incompatible with fast equilibration. However, in order to see averaging "on the NMR time scale", the molecules must be able to sample both chemical environments. If the clusters are isolated from the exterior by the macroscopic dimensions of Nafion particles, then fast diffusion within the two environments can occur, but interchange between the two different phases may be slow.

Resonances from internal and external water are also seen when "bench-dried" Nafion-H is swollen in aqueous acetonitrile. In solutions containing <10% H_2O by volume, no external water is seen; the limiting chemical shift for internal water is 8.4 ppm.

C. Development of a Protocol for Measuring the Water Content Quantitatively. In principle, the water content of the polymer could be estimated quantitatively by measuring the area of the OH resonance and comparing it with that of a reference substance added in known molar amount. NMR has an advantage over other spectroscopic techniques for quantitative measurements in that all nuclei of a given type (e.g., protons) may be assumed to have the same extinction coefficient. Then the area ratio of OH protons to reference protons is the same as their mole ratio.

The approach is as follows. The solvent contains a known molar amount of "reference" protons. A weighed amount of Nafion of known equivalent weight is swollen in a weighed aliquot of solvent. The mixture is heterogeneous, and so measuring the area ratio presents a problem that does not arise in homogeneous solution. In homogeneous solution, the spectrometer can sample a portion of the total material in the NMR tube; this may reasonably be assumed to be representative of all the material. For heterogeneous samples, it is imperative that the internal (OH) and the external solvent (reference) protons are sampled with equal sensitivity. In practical terms this means that the whole of the sample must be located within the center one-third or so of the receiver coils of the NMR spectrometer. Most single-frequency probes for proton NMR have relatively small radio-frequency coils (3 mm or so). For this reason, a double-tuned probe for multinuclear observation on a Bruker WH 400 instrument was used because the proton decoupling coils of the 10-mm probe are 27 mm in length and these could be used as detector coils. This is generally true for most decoupling coils.

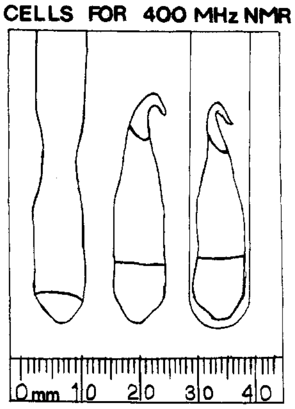

Figure 1. Cells for 400-MHz NMR. Left to right: empty cell plus Nafion-H powder; swollen powder with cell sealed under vacuum; homemade cell inside standard 10-mm NMR tube.

The samples were prepared in homemade cells (Figure 1) that were constructed out of standard-wall 8-mm-o.d. Pyrex tubing. A sample whose height was not greater than 10 mm was prepared in the swelling solvent and sealed under vacuum. The assembly was then slid into a standard 10-mm NMR tube and positioned so that the sample was completely contained within the central portion of the spectrometer coils. Because the resonances of the heterogeneous samples were inherently broad, there was no need to spin the samples. However, it was necessary to shim the magnetic field individually for each sample because the homemade cells were not symmetrical or identical in shape. As expected, the degassed samples had longer than usual relaxation times, and it was necessary to use appropriately longer pulse delays to ensure complete recovery of the magnetization between pulses, otherwise all the proton nuclei in the samples would not have been detected with equal sensitivity.

D. Quantitation of the Water Content of Nafion Samples Swollen in D_2O. Heavy water is a particularly suitable choice for making quantitative measurements. As will be seen in section E, hydrocarbon-swelling solvents have the disadvantage that at low water content the OH resonances are broad and difficult to integrate. In D_2O, the proton resonances remain sharp at all H_2O contents because the water present in the Nafion exchanges with the D_2O solvent. The areas of both internal and external HDO must be included in the total proton count after subtraction of any HDO impurity originally present in the solvent. In order to have a reference substance available for relating areas, a known quantity of acetonitrile was added to the solvent. The proton composition of the solvent (both CH_3CN and residual HDO) was assayed separately, see Experimental Section.

A total of 43 Nafion samples of widely differing composition were analyzed by the NMR method. We first measured the OH content of the samples in the reference state (section A). These were found to contain three hydroxyl protons for each sulfonate group. The reference state is thus the monohydrate of Nafion-H, which can best

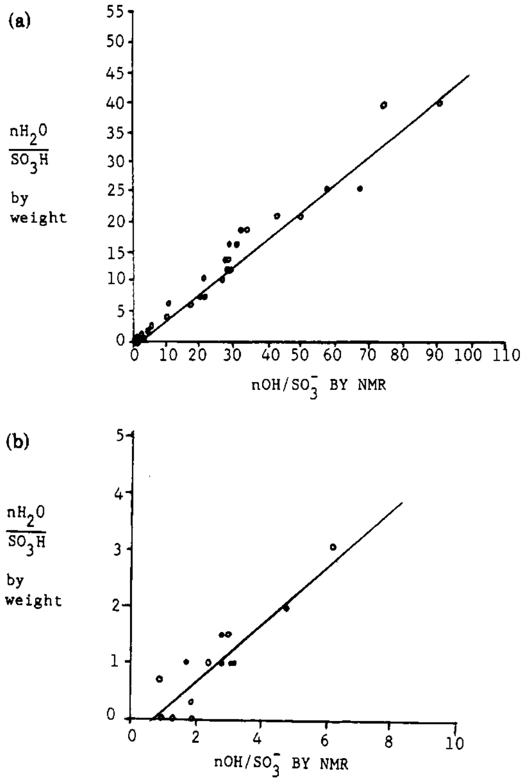

Figure 2. Relationship between moles of OH determined by NMR and water loss: (a) all samples; (b) drier samples only. Solvent was D_2O.

be represented as the H_3O^+ salt, i.e., $R_FSO_3^-\cdot H_3O^+$. The absolute water content of the other samples was then determined by the difference in mass between the sample and the reference state, assuming the mass differences to be due entirely to the loss or gain of water.

The data are plotted in Figure 2a, where the abscissa is the proton content determined by NMR and the ordinate is the absolute water content determined as described in the previous paragraph. Figure 2a gives all the data, while Figure 2b encompasses only the drier samples. We note the following points:

1. The slope of the line is 0.46 ± 0.02 (all samples) or 0.48 ± 0.04 (low-water samples). The slope of the line should be 0.50 if all the mass loss is due to water. Thus the NMR analytical method parallels the mass loss measurements satisfactorily.

2. Each individual NMR determination is subject to considerable uncertainty, as a result of factors such as peak asymmetry, need for baseline correction, etc. The relationship could only be validated by the expedient of having a large number of determinations.

3. When Nafion is dried at elevated temperatures, it loses water beyond the reference state. This further weight loss amounted to 1.3–1.7% by mass at temperatures in the range 100–200 °C and pressures of 10^{-2}–10^{-3} torr.[12] The Nafion-501 that was used has equivalent weight 1200, so that 1.5% represents 18 g mol^{-1} (≡1 H_2O). Thus the material dried at elevated temperature is the free sulfonic acid. The intercept of Figure 2, parts a and b, appears on the ordinate at ca. −0.5 H_2O per sulfonate. This point (zero protons by NMR) represents the sulfonic anhydride; we did not reach this composition in any of our experiments.

4. As noted in section B, Nafion powder takes up considerable amounts of water when it is swollen in water, especially at higher temperatures. Typical analyses for the swollen material are as follows: swollen in cold water (25 °C); $\sim R_FSO_3H\cdot 21H_2O$; boiled in water, $\sim R_FSO_3H\cdot 25H_2O$; heated at 170 °C (sealed tube), $\sim R_FSO_3H\cdot 40H_2O$. Previous workers[5,11] have estimated that Nafion-H of equivalent weight 1200 takes up about 30% water by weight when it is boiled in water, in line with our results.

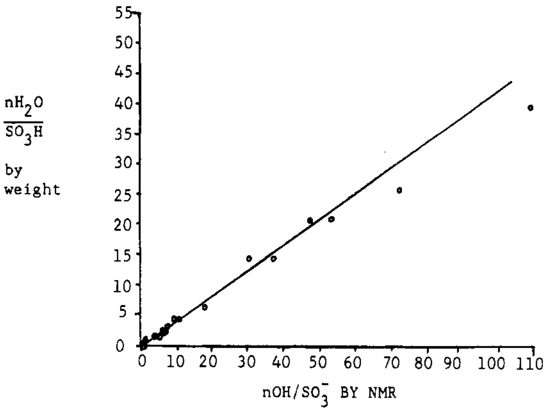

Figure 3. Relationship between moles of OH determined by NMR and water loss in cyclohexane as swelling solvent.

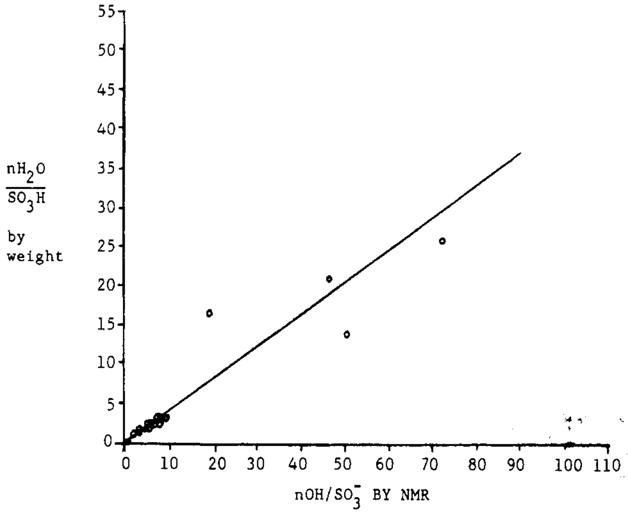

Figure 4. Relationship between moles of OH determined by NMR and water loss in benzene as swelling solvent.

E. Quantitation of the Water Content of Nafion Samples Swollen in Benzene-d_6 and Cyclohexane-d_{12}. In these cases, the proton reference was the residual protons in a known amount of benzene-d_6 (or cyclohexane-d_{12}) that was added to the solvent and standardized by NMR with *sym*-tetrachloroethane as a standard. Samples of Nafion-H, calibrated for water content by mass relative to reference state, were swollen in the hydrocarbon and then studied by NMR. In these two solvents, both chemical shift and peak area information could be obtained.

Quantitatively, a linear relationship between the NMR resonance area due to OH protons and the relative mass differences due to water was again observed. Figures 3 and 4 are analogous to Figure 2. For reasons discussed below, the quantitation is less satisfactory in these solvents than in D_2O; the slopes of the lines are 0.43 ± 0.03 (intercept −0.4) in cyclohexane and approximately 0.4 in benzene.

In cyclohexane, the experimental difficulties were most severe at low water content. Lowering the water content causes the OH resonance to broaden as well as to shift downfield, and its area becomes difficult to determine. Compounding this, there seems to be a definite trend at $n(OH)/n(SO_3^-) < 7$ for the line to deviate such that the NMR determination shows fewer moles of OH than are predicted by the mass loss experiments. A possible explanation of this effect is that at these low water contents,

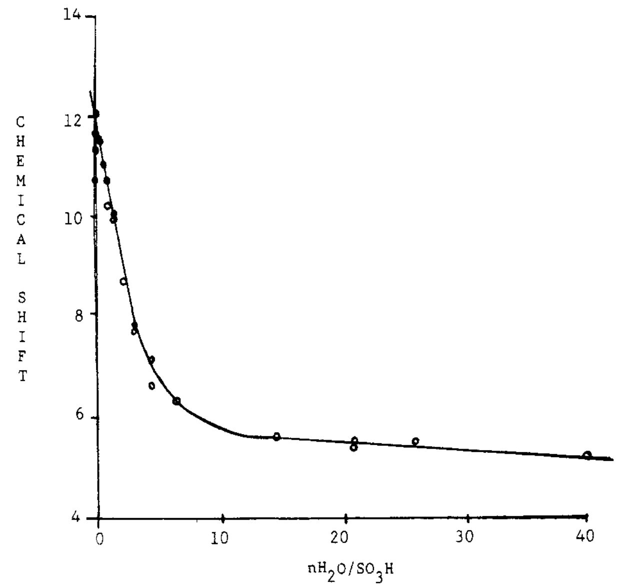

Figure 5. Chemical shift of OH resonance vs. water content in cyclohexane as swelling solvent.

some of the water molecules are held in essentially rigid environments, and their resonances become too broad to detect by the high-resolution NMR techniques used. (When these same samples are examined in D_2O, their NMR behavior is normal, and the points fall on the line shown in Figure 2.)

The major problem encountered when benzene was the swelling solvent was that at many levels of hydration the chemical shifts of benzene (7.3 ppm) and the hydroxyl resonance were close and the peaks overlapped. Consequently, the spectrum had to be resolved into its components with a curve-fitting procedure. This was difficult to do reproducibly, especially at the lower water contents, as the OH resonance was once again broad. At the lowest water contents of all (Nafion-H dried at elevated temperatures), the disparity in peak shapes made the computer simulations not meaningful.

An additional minor problem with benzene as the solvent is that Nafion-H is capable of exchanging the benzene isotopically.

$$\text{Nafion-SO}_3^-\text{H}^+ + \text{C}_6\text{D}_6 \rightarrow \text{Nafion-SO}_3^-\text{D}^+ + \text{C}_6\text{D}_5\text{H}$$

This does not affect the positions of any of the resonances but it changes the hydroxyl:reference area ratio. Fortunately, exchange does not occur at room temperature to any extent over the course of 1–2 h; it does occur if the samples are left to stand for several days, but the difficulty is easily circumvented either by running the spectra directly after sample preparation or by freezing the samples in liquid nitrogen if access to the spectrometer is not possible immediately.

F. Chemical Shift Scale for Water Content. The relationship between weight change and NMR resonance area in D_2O effectively calibrates the weight change scale (Figure 2), and this relationship may thus be taken as established. Therefore it is possible, in either benzene or cyclohexane, to set up a relationship between weight change and chemical shift. (There are obviously no shifts in the H_2O/D_2O system.) Figures 5 and 6 show the relationship between weight change, expressed as water molecules per SO_3H residue, and chemical shift of the hydroxyl resonance in cyclohexane and benzene respectively.

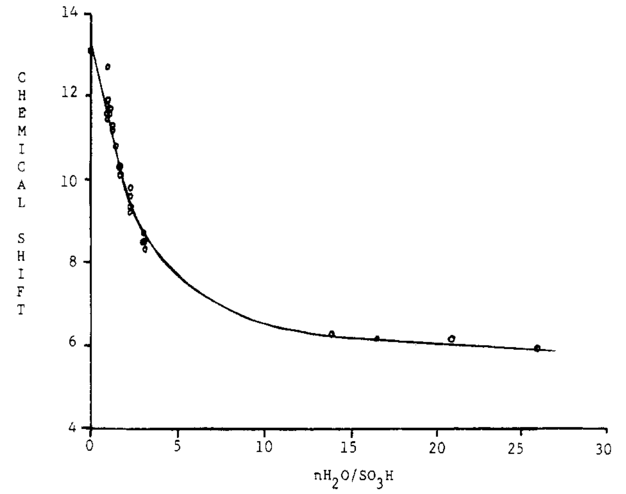

Figure 6. Chemical shift of OH resonance vs. water content in benzene as swelling solvent.

In the range $n_{H_2O}/n_{SO_3H} > 10$ the chemical shift changes very little with water content, and so the chemical shift value is not very diagnostic of the composition. However, in this range, the water content may be very easily determined simply by drying the sample to constant weight, with very little error, since the weight change is substantial. In the more difficult range $n_{H_2O}/n_{SO_3H} < 10$, the chemical shift changes sharply with water content in both solvents and the chemical shift thus becomes a very sensitive measure of the water content. Figures 5 and 6 thus represent calibration curves of chemical shift vs. water content. We note that for the determination of chemical shift alone, it is not necessary to use a spectrometer having the large detector coils that were essential for quantitative determination; almost any spectrometer will suffice, subject to the limitation that at low water content the OH resonance will be broad and of low intensity. We were unable to detect the signals at the lowest water content using a simple CW instrument (Varian EM 360).

Conclusion

We have established a method of determining the water content of Nafion-H directly by ^{1}H NMR. The method should be applicable with minor modification to other hydrated polymers. The quantitative (integration of peak areas) method for measuring the water content is not simple to carry out in practice, as it requires careful experimental technique, and even then the uncertainties in any one individual determination are such that several replicate analyses would be needed for one to have confidence in the result. However, now that this calibration has been established, the relationship between chemical shift and water content in solvents such as deuterated cyclohexane or benzene can be used to estimate the water content of a particular Nafion-H sample simply by swelling a portion of the Nafion in the chosen solvent and making a single chemical shift determination.

Equally importantly, we have established an easily obtained and reproducible reference state (Nafion-H dried to constant weight in vacuo at room temperature) and determined it to be the monohydrate, i.e., $R_FSO_3^-{\cdot}H_3O^+$. Mass differences between any sample and the reference state may be used to determine the water content of the sample absolutely.

Experimental Section

Nafion-501 powder was obtained from Du Pont as the potassium salt. It was converted to the acid form by five exchanges with 2.5 M hydrochloric acid at room temperature, as described in the Du Pont bulletin. For each exchange the Nafion was stirred in the acid for several hours, sometimes overnight, and then filtered. After the final filtration, the Nafion beads were washed thoroughly with deionized water. The washing was considered complete when no precipitate formed on addition of silver nitrate solution to the wash water.

The titrations of Nafion to determine the equivalent weight were performed with a 0.02 M solution of potassium hydroxide in 95% ethanol. A weighed sample of Nafion-H (about 200 mg) was soaked at about 70 °C in 25 mL of a 4% NaCl solution for 30 min before titrating in order to partially convert Nafion-H to Nafion-Na and thereby minimize the time required for the titration. The titration was carried out with a stoppered pressure equalizing buret and the endpoint determined with phenolphthalein as the indicator. Complete neutralization was considered to have occurred when the indicator-determined "end point" was stable for 15 min.

The weight-change experiments were done on two standard all-glass vacuum racks, each equipped with a mechanical oil pump and an oil diffusion pump. The experiments at 10^{-4} or 10^{-5} torr were done with a three stage oil diffusion pump, while those at 10^{-2} or 10^{-3} torr were done with a two-stage oil diffusion pump. For drying at room temperature, the Nafion samples were contained in Pyrex glass ampules that were attached directly to the vacuum rack with greaseless "O-ring" joints. The samples were frozen in liquid nitrogen prior to evacuation in order to avoid "bumping" during the initial outgassing. Drying of Nafion at elevated temperatures was done in a glass drying pistol. The Nafion was placed in 8-mm-o.d. Pyrex tubes that were sealed at one end and plugged with glass wool at the other. Four to six tubes could be placed in the drying pistol at any time. Solvents and temperatures used in the drying pistol were water, 100 °C; bromobenzene, 156 °C; 1,3-dichlorobenzene, 170 °C; ethyl malonate, 199 °C; 2,5-dimethylaniline, 218 °C; 1-chloronaphthalene, 250 °C. Prolonged heating of Nafion-H at 100 °C under vacuum produced a barely discernible darkening of the beads. Darkening was significant at higher temperatures. Above 200 °C the Nafion became charred and the particles caked together. In parallel mass spectrometric experiments, no ions other than those assignable to water could be observed below 170 °C; above this temperature an ion (possibly due to SO_2) appeared at m^+/e 64. It became more intense as the temperature was raised, especially above 220 °C. Above this temperature m^+/e 19 and 20 (F and HF?) also became prominent. We conclude that drying Nafion at temperatures above 170 °C results in at least partial decomposition.

Drying to constant weight under vacuum at $T \geq 100$ °C affords Nafion-H having one or fewer H_2O molecules per sulfonic acid. At the other end of the range, the most highly hydrated materials were obtained by soaking the Nafion-H in water; the compositions of these materials are recorded in section D of Results and Discussion. For Nafion heated in sealed tubes at 170 °C, the weight change was found by determining the weight gain upon weighing the Nafion before adding water and again after filtering off the excess water after heating the samples for 2 h. These high-pressure experiments were performed in heavy-wall 8-mm-o.d. Pyrex tubes that were filled with about 1 g Nafion and enough water to provide a column of water 2 or 3 cm above the level of the Nafion in the tube before heating. After heating the sample, only a slight excess of liquid water was visible.

Nafion-H samples of intermediate water content (5–20 H_2O per sulfonate) were prepared from the water-soaked material by partial dehydration under vacuum at room temperature. All weight-loss experiments were done at least in duplicate; more often 3–5 replicates were studied.

Qualitative NMR Experiments. ^1H NMR spectra were obtained at 60 MHz. A Varian EM360 was used for most of the experiments at ambient temperature, but a Varian T60 and a Bruker WP 60 were used occasionally with similar results. Variable-temperature experiments were done on a Varian A60A. For the spectra on the Varian EM360, the most commonly used parameters were as follows: 10 ppm sweep width; 2 min sweep time; filter time constant = 0; radio-frequency power 0.3–0.4 mG. Prior to use, the spectrometer was locked and shimmed on tetramethylsilane in chloroform solution, but the actual Nafion spectra were run with the spectrometer unlocked. The samples were generally prepared in standard, thin-wall NMR tubes. Medium-wall tubes were used when it was necessary to seal the tubes. The samples were 1–2 cm in depth, at least twice the length of the receiver coils on the EM360 (which are 0.6 cm long). It was found that the easiest way to fill standard NMR tubes with swollen Nafion was to add the solvent first and then pour in enough dry Nafion to fill the tube to a height of at least 1 cm. To ensure that the samples were fully swollen, a visible excess (at least 1–2 mm) of solvent was always present; the samples were generally allowed to equilibrate for $^1/_2$ h before the spectra were run.

In aqueous acetonitrile containing less than 75% by weight water in the solvent, peak widths at half height were 20–25 Hz for internal water, acetonitrile, and external water when it was present. In pure H_2O, D_2O, or in acetonitrile with more than 75% water the peaks were considerably sharper, 4–5 Hz for internal water and 8–10 Hz for external water. In CH_3OH/CCl_4, the resonance(s) due to OH protons were 5–10 Hz at half-height in samples with more than 5% methanol by volume. In samples with less than 5% methanol the peak due to the hydroxyl protons was considerably broader, ca. 25 Hz. The peak due to the methyl protons was 5–10 Hz at half-height at all methanol concentrations.

Quantitative NMR Experiments. The spectra were run on a Bruker model WH 400 spectrometer. A 5-μs pulse (ca. 10° magnetization tilt) applied to the decoupler coil of a double-tuned 10-mm multinuclear probe was used with a 20-s pulse delay to ensure that all species were detected with equal intensity. An 8K block size was used, and a 35 kHz sweep width was used for dry ($nH_2O/SO_3H < 3$) samples in benzene or cyclohexane, but narrower sweep widths were used with wetter samples or for samples swollen in D_2O (10 000 Hz). It was necessary to subtract the background carefully in order to obtain a flat baseline, since resonances from the probe and the glass cell were detected when the very wide sweep widths were used. The background spectrum of an empty cell was obtained on every occasion that measurements were made, using the same parameters and shim settings used to obtain the spectra of the Nafion samples. The FID of the background was subtracted by computer before transforming the spectrum of the Nafion sample. The line-broadening function used depended on the signal intensity, which was determined by the proton concentration of the solvent, the degree of hydration of the Nafion, and the sample size. The maximum line broadening used was 50 Hz. At 400 MHz, this introduces little peak distortion, only $^1/_8$ ppm. Since the spectra in cyclohexane and benzene were generally between 500 and 3500 Hz at half-height, this was not a significant effect. For the spectra of Nafion in D_2O, 10–20 Hz line broadening was generally sufficient. Spectra in water or cyclohexane were integrated with the Aspect computer on the WH 400. For spectra in benzene, computer simulation of the spectrum was performed on an Ohio Scientific Challenger 8P-DF computer with a Hewlett-Packard Model 7202A graphic plotter. The program was written by Uwe Oehler and used visual fitting of the actual spectrum to a Lorentzian curve.

The samples for quantitative measurements were prepared in homemade coaxial cells (Figure 1) made of 8-mm-o.d. Pyrex glass. These cells were dried in the oven at 100 °C overnight and then stoppered tightly while they cooled to room temperature. The cells were filled by first weighing them, adding the Nafion through a small long-stemmed funnel so that the powder went right to the bottom of the cell, rather than adhering to the walls, weighing, adding the solvent with a 100-μL Hamilton syringe, and weighing again. The cells were then placed on a vacuum rack, frozen in liquid nitrogen, and degassed. The stopcock to the pump was then turned off and the samples were quickly sealed with a flame after removing the liquid nitrogen bath. Any solvent adhering to the walls of the tube above the constriction was chased down with a cool flame while the sample was frozen before evacuation, this procedure being especially necessary when the solvent was D_2O. To keep the Nafion in the bottom of the tube while it was being weighed, it was important to keep the tubes as near vertical as possible. The tubes were generally too tall to stand vertically in the balance, and a styrofoam cup with holes punched in the sides was used to support them.

Nafion Swollen in D_2O. The quantity of acetonitrile added as a reference and the residual HDO were determined with sodium pyruvate in the same manner as the protiobenzene concentration in deuteriobenzene was determined with tetrachloroethane (see below). When all of the solvent was not used immediately, it was stored in a sealed tube and restandardized before use. For very dry samples, nominally 100% deuterium oxide was used. This

Table II
Spectral Data on Nafion-H Swollen in D_2O with Added CH_3CN

nH$_2$O/SO$_3^-$ by wt (absolute)	nOH/SO$_3^-$ by NMR	nH$_2$O/SO$_3^-$ by wt (absolute)	nOH/SO$_3^-$ by NMR
4.5	10	6.6	11.7 ± 2
4.5	10.5 ± 0.5	21	43 ± 4
3.1	6.1 ± 0.1	21	50 ± 4
3.1	9.0 ± 1.5	16	26
2.0	4.9 ± 0.5	16	29
2.0	6.6 ± 1	13	28
1.5	3.0 ± 0.1	13	27
1.5	3.0 ± 0.3	7.8	21.1 ± 2
1.0	2.4 ± 0.4	7.8	20
1.0	1.7 ± 0.1	6.5	18 ± 1
1.0	2.8 ± 0.6	6.5	17 ± 3
0.6	0.9 ± 0.05	40	91 ± 10
0.3	2.4 ± 0.5	40	75 ± 10
12.3	28 ± 2.3	1	3.1
12.3	29 ± 2.0	1	3.5 ± 0.5
0.7	3.3 ± 0.3	25	57 ± 6
0	1.5 ± 0.3	25	67 ± 5
19	32 ± 3.5	0[a]	1.9 ± 0.3
19	34 ± 4	0[a]	1.0 ± 0.1
11	21 ± 2.5	0[b]	1.9 ± 0.2
6.6	13 ± 1.5	0[b]	1.3 ± 0.3

[a] Dried at 170 °C. [b] Dried at 100 °C.

Table III
NMR Data on Nafion-H Swollen in Cyclohexane-d_{12}

nH$_2$O/SO$_3$H by wt	nOH/SO$_3^-$ ± error	δ_{OH}	ω_{OH}[a]	ω_{CH}[a]
1.0	1.2 ± 0.1	10.7, 10.8 ± 0.5	3200	680
1.0	1.1 ± 0.1	10.1, 10.4 ± 0.5	2400	880
2.3	6.9	8.7 ± 0.1	360	600
2.3	6.3	8.7 ± 0.1	400	560
1.5	3.9 ± 0.4	9.8 ± 0.3	880	600
1.5	5.5 ± 0.6	9.9 ± 0.3	887	880
3.1	7.7 ± 0.8	7.8 ± 0.2	400	640
3.1	7.4 ± 0.7	7.7 ± 0.3	400	600
21	47 ± 5	5.5 ± 0.2	370	390
21	53 ± 6	5.4 ± 0.2	290	500
14.6	30 ± 3	5.6 ± 0.3	230	540
14.6	37 ± 4	5.6 ± 0.2	460	375
4.5	11 ± 0.7	6.6 ± 0.2	230	315
4.5	9.5 ± 1	7.1 ± 0.3	270	440
0.60	0.6 ± 0.03	11 ± 0.5	3260	480
0.27	0.27	11.5 ± 0.5	3900	450
6.5	18	6.3 ± 0.1	250	730
40	109 ± 10	5.2 ± 0.1	250	400
26	72	5.5 ± 0.2	350	440
0	0.79 ± 0.04	10.7 ± 0.3	2600	480
0	0.74	11.3	very broad	
0	0.64	11.6	very broad	

[a] Width (Hz) at half-height.

Table IV
NMR Data on Nafion-H Swollen in Benzene-d_6

nH$_2$O/SO$_3$H by wt	nOH/SO$_3$H by NMR	δ_{OH}	ω_{OH}[a]	$\omega_{benzene}$[a]	$\omega_{C_6H_{12}}$[a]
1.0	2.1	11.6	3400	400	
1.0	1.9	11.8	2700	460	
1.0	1.7	11.8	3300	720	
1.0	1.8	11.8	3100	410	
0	0.07	13.1	3600	600	
2.3	4.6	9.2	550	550	
2.3	6.0	9.2	970	460	
2.3	6.7	9.8			
2.3	6.7	9.8			
2.3	5.6	9.6			
1.7	4.4	10.3			
1.7	5.5	10.3			
1.7	4.1	10.1			
3.1	9.1	8.5			
3.1	7.6	9.7			
1	1.2	11.9	3000	450	500
1	1.2	11.9			
1.2	1.6	11.6	2500		770
1.2	1.9	11.7	2800		670
1.3	2.9	11.2	1400		560
1.3	3.2	11.3	960	770	480
1.5	2.6	10.8	930		540
1.5	3.1	10.8			
2.3	7.5	9.3	800		900
2.3	5.8	9.3	610		420
3.2	7.2	8.5	290		480
3.2	6.9	8.3	350		384
1.0	1.2	11.5	3100		650
1.0	1.4	12.7	3000		500
21	46.2	6.2			
17	18.8	6.2			
14	50.5	6.2			
10.5	*b*	6.5			
7.8	*b*	6.6			
6.5	*b*	~7			
40	*b*	6.0			

[a] Width at half-height; when no value is given, the overlap between the benzene and the hydroxyl protons was too great to allow accurate measurement. [b] OH and C_6H_6 peaks not resolvable.

was found to have a residual water content of 1.1 × 10^{-4} mol of H/g and an acetonitrile content of 1.7 × 10^{-3} mol of H/g after addition of acetonitrile. For very wet samples, acetonitrile concentrations as high as 30% were used. The samples were prepared and run as described for cyclohexane and benzene. Although the samples were frozen in liquid nitrogen prior to sealing the cells, the cells did not crack, there apparently being enough space in the Nafion beads to allow for expansion of the water on freezing.

The original data on which Figure 2 is based are recorded in Table II.

Nafion Swollen in Cyclohexane or Benzene. For samples containing less than 2 H_2O/SO_3H there were enough residual protons in the deuterated cyclohexane or benzene to provide a convenient reference peak. For wetter samples some protiocyclohexane or -benzene was added so that the reference and hydroxyl peaks were of comparable height. When the solvent was benzene and the samples were dried at elevated temperature, it was necessary to use isotopically very pure (99.96%) benzene to distinguish the hydroxyl peak from the overlapping benzene peak. Both benzene and cyclohexane were standardized by ^1H NMR with *sym*-tetrachloroethane as a reference for solvents with proton contents less than 10%. Higher proton contents were determined by weight alone. A typical standardization (one of a minimum of three) of proton-enriched deuteriobenzene was conducted as follows. Tetrachloroethane (0.0267 g, 3.178 × 10^{-4} mol H) was placed in a standard 5-mm NMR tube. The benzene solution (0.2908 g) was added. The NMR spectrum was run on the EM 360 and the integrated ratio of benzene to tetrachloroethane (TCE) was found to be 0.40 (average of three integrations).

The original data on which Figures 3 and 4 are based are recorded in Tables III and IV.

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Registry No. Nafion-H, 63937-00-8; Nafion-501, 62563-55-7; water, 7732-18-5.

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(12) Prolonged heating (10–50 h) was required to reach constant weight, and it seems likely that the reference states chosen by some of the previous workers do not represent equilibrium. Above about 200 °C extensive decomposition occurred.

Acidity and Catalytic Activity of Nafion-H

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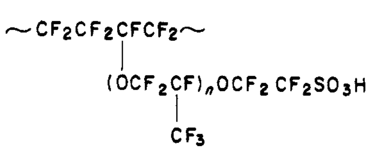
ABSTRACT: Studies with acid–base indicators have shown that suspensions of the fluorinated sulfonic acid polymer Nafion-H behave as an acid of strength comparable with CF_3SO_3H, but only in solvents capable of removing the water chemically from within the beads. The proton NMR spectra of Nafion-H samples swollen in benzene or cyclohexane show that the chemical shift of the hydroxylic protons moves downfield as the water content decreases. The observed chemical shift arises from fast exchange between H_2O and the Nafion-H and indicates that samples having the ratio $OH/SO_3^- \geq 3$ behave as $R_FSO_3^-{\cdot}H_3O^+$ ion pairs in the interior of the beads. Nafion-H samples similar to those used by other workers for catalysis of organic reactions have the approximate composition $R_FSO_3^-{\cdot}H_3O^+$, where the catalytically active species is the unsolvated $R_FSO_3^-{\cdot}H_3O^+$ ion pair. This explains the great acidity of these catalysts, which is comparable with concentrated (>95%) solutions of H_2SO_4. Catalysis of hydrogen–deuterium exchange in aromatic compounds by Nafion-D/D_2O is found to be of only limited application.

Introduction

Nafion-H, the acidic form of the polymeric fluorinated sulfonic acid 1, has been widely investigated as an acidic catalyst for organic reactions.[1] All indications are that



$$\begin{array}{l}\sim CF_2CF_2\underset{|}{C}FCF_2\sim \\ \quad (OCF_2\underset{|}{C}F)_nOCF_2CF_2SO_3H \\ \qquad\;\; CF_3\end{array}$$

1

the substance is a very strong Brønsted acid. Thus Nafion-H catalyzes the isomerization of dialkylbenzenes in the gas phase at elevated temperatures, with an activity intermediate between that of SiO_2/Al_2O_3 ($H_0 = -8$) and that of $AlCl_3$ in solution ($H_0 = -15$).[2] Similarly, in the formation of phenylphosphorus dichlorides from PCl_3 and substituted benzenes, Nafion-H has a catalytic activity comparable with that of Brønsted acids having $H_0 < -12$.[3] To date, no reports on the direct determination of an effective acidity constant for Nafion-H have appeared or on the effect of traces of water on its acidity. This is the purpose of this study.

Results and Discussion

Indicator Studies. The determination of an effective pK_a for Nafion-H is not straightforward because Nafion-H is not soluble in water or organic solvents at room temperature.[4] In a heterogeneous suspension of Nafion-H in water, the pH of the aqueous phase is not affected by the presence of Nafion-H. This can be shown by dipping a piece of pH paper into the slurry: a color change is observed only where the paper is in contact with the Nafion-H beads.

Protonation of Hammett indicators[5] by suspensions of Nafion-H was shown by observing the beads acquire the color of the protonated form of the indicator. For example, when a yellow aqueous solution of *p*-aminoazobenzene is shaken with Nafion-H, the beads become red and the solution decolorizes. Addition of aqueous NaOH to the separated aqueous phase effects no color change, but addition of the filtered beads to this reagent decolorizes the beads and regenerates yellow in the supernatant liquid.

In water, Nafion-H completely protonated bases at least as basic as *p*-nitroaniline ($pK_a = 1.0$), partially protonated *o*-nitroaniline ($pK_a = -0.3$), and did not protonate 4-chloro-2-nitroaniline ($pK_a = -1.0$) to a detectable extent. Homogeneous aqueous solutions of *p*-toluenesulfonic acid ($pK_a = -5$ to -7)[6] behaved similarly to the Nafion-H suspensions.

An experiment to determine an effective K_a for Nafion-H in water was carried out by partitioning a known amount of organic base (*o*-nitroaniline) between bulk water and the beads. The loss of dye from the bulk solution was measured spectrophotometrically. An order of magnitude estimate of K_a for Nafion-H was obtained from equilibria 1–3 by making the further assumptions (i) that the concentration of the uncharged indicator is the same in the "internal" water as it is in the bulk, (ii) that K_a for the indicator is the same in the internal environment, and (iii) that equilibrium is reached during the time of the experiment (~25 min). The equilibrium constant for reaction 3 was found to be 2.2, in remarkable agreement with the value of unity would be expected if the acidic species in 1 and 3 were actually H^+_{aq} and not the neutral R_FSO_3H.

$$R_FSO_3H + In \rightleftarrows R_FSO_3^- + HIn^+ \qquad K_1 = K_{obsd} \quad (1)$$

$$HIn^+ \rightleftharpoons H^+_{aq} + In \qquad K_2 = K_a \text{ for } HIn^+ \quad (2)$$

$$R_FSO_3H \rightleftharpoons R_FSO_3^- + H^+_{aq} \qquad K_3 = K_a \text{ for } R_FSO_3H = K_1K_2 \quad (3)$$

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