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ARTICLES

Water in Perfluorinated Sulfonic Acid Nafion Membranes

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We have studied water contained in the perfluorinated sulfonic acid (denoted as RSO_3H) membrane by FT-IR spectroscopy. The IR spectra of the membrane, which absorbed water quickly even from the air, changed so drastically during dehydration that they showed clearly two isosbestic points in the 4000−1500 cm^{-1} region. Analysis of the IR spectral changes made it clear that water molecules exist mostly as H_3O^+ in equilibrium with RSO_3^- and RSO_3H in the membrane. The IR change accompanying dehydration was found to result from the reaction as $RSO_3^- + H_3O^+ \rightarrow RSO_3H + H_2O$(evaporating out). The IR spectrum of H_3O^+ was clearly separated, which shows a broad OH stretching absorption with two unseparated peaks around 3370 and 3120 cm^{-1} and an OH deformation absorption at about 1720 cm^{-1}. The spectrum is distinctively different from that of water separated, coexisting with H_3O^+, RSO_3^-, and RSO_3H in the membrane, which shows OH stretching and deformation absorptions at about 3480 and 1628 cm^{-1}, respectively.

Introduction

The Nafion membrane, which is a name commonly used for perfluorinated polymeric sulfonic acids[1] developed by E. I. du Pont Nemours Co., Inc., is indispensable electrode material for fuel cells. It is well-known that water in the membrane is crucially important for its electrochemical activity. To understand the function of water contained therein is not only a subject of chemical interest but also of great importance for advanced applications of the membranes.

Many studies have been carried out on water in the membrane by the use of IR,[2−5] NMR,[6−8] neutron-diffraction,[9] and positron-annihilation spectroscopy.[10,11] Infrared spectroscopy is powerful to study water, because the spectrum is very sensitive to the structure. Ostrowska and Narebska[5] found that the infrared spectra changed drastically, depending on the water content, but the changes were not reasonably interpreted. Sondheimer et al.[7] found that the suspension of Nafion particles of the acid form is as strongly acidic as CF_3SO_3H. Water in the Nafion membrane has been long studied, but the interactions of water with Nafion membranes have not been well understood yet. In the present paper, we have found that drastic spectral changes of the membrane caused by dehydration originate from the decomposition of H_3O^+ in equilibrium with RSO_3H and RSO_3^- with the release of water.

Experimental Section

The Nafion112 (50 μm thick) and Nafion NR111 (25 μm thick) samples used in the present study were commercially obtained as the acid type. The sample of the sodium salt type was prepared by the treatment of the original membrane in a NaOH solution of 1.0% concentration. Some of the membrane was treated serially with hydrogen peroxide solution (3 wt %) at 100 °C, boiling water, sulfuric acid solution (1 mol/L) at 100 °C, and finally cleaning in boiling water, the time of each treatment being for 1 h.

A Nafion membrane of an acid or a salt type easily absorbs an appreciable amount of water from being in the open air.

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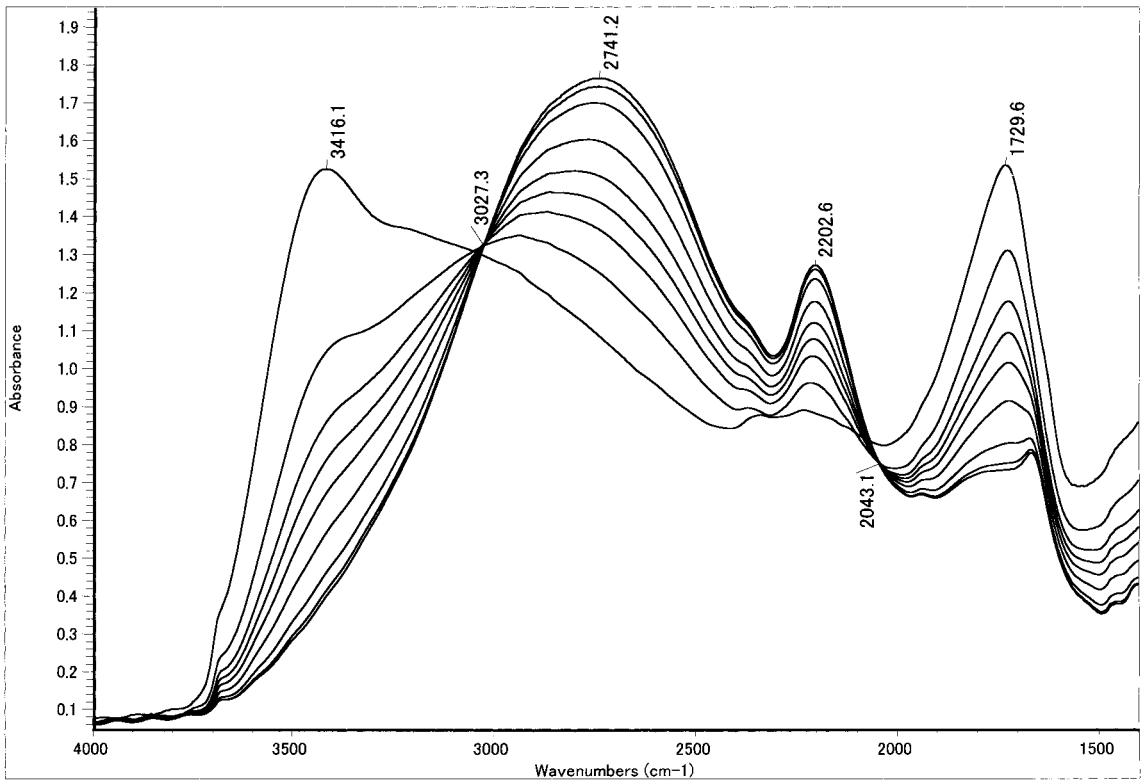

Figure 1. A series of FT-IR spectra of a treated Nafion112 membrane of the acid type during dehydration, starting from a sample stored in the open air. The dehydration proceeds from the top to the bottom at the frequencies of 3416 and 1730 cm^{-1}, and each of the spectra is denoted alphabetically as a (0), b (1 min 51 s), c (3 min 42 s), d (5 min 28 s), e (8 min 5 s), f (14 min 27 s), g (35 min 8 s), h (64 min 8 s) and i (138 min 39 s) from the top to the bottom at the frequencies, where the time lapse after the start of the measurements is given in parentheses. The time proceeds in the opposite direction or from the bottom to the top, for the two peaks at 2741 and 2203 cm^{-1}. A spectrum is referred to by the above alphabetic notation in the text as spectrum a of Figure 1, for example. Spectrum a, which only does not pass through the isosbestic points, is at the lowest between about 3000 and about 2100 cm^{-1}, while the above-mentioned four absorptions in all of the other spectra change in intensity simply upward or downward with the progress of dehydration, changing the direction passing an isosbestic point. The ordinate is the same for all of the spectra.

Infrared spectra were usually measured for a sample that was stored in the open air. To obtain a sample containing more water, it was immersed in water at room temperature for about 10 min just before the measurement. To follow the infrared spectra of a Nafion membrane during dehydration, the spectra were successively and intermittently measured for the sample, which was kept held at a film holder in the spectrometer all through a whole measurement, to the possibly most dehydration under the purge of dry air. Water in the membrane quickly evaporates especially at first under the flow of dry air, as is seen from the spectral changes shown in Figure 1, in which the time lapse after the start is given for each spectrum.

The FT-IR spectrometer used in the present study was a Nicolet Magna 760 equipped with a DTGS detector and a KBr beam splitter. A spectrum was normally measured with a resolution of 4 cm^{-1} and 50 scans.

The spectrum of liquid water was measured for water sandwiched between two flat KRS-5 plates without a spacer.

Results and Discussion

Figure 1 shows a series of infrared spectra of a Nafion112 membrane in the 4000−1400 cm^{-1} region during dehydration. The spectral feature observed in Figure 1 was well reproducible, and the same spectral changes were observed both for the as-received sample and the one treated as described in the Experimental Section. The series of the spectra shows drastic changes following dehydration. The membrane has an absorption at 3416 cm^{-1} with a broad shoulder around 3000 cm^{-1} tailing down to about 2400 cm^{-1} and a strong absorption at 1730 cm^{-1}, together with some absorptions in the 2300−2100 cm^{-1} region at the first measurement, as shown in spectrum a of Figure 1. By dehydration to the second measurement, the absorption at 3416 cm^{-1} decreases in intensity abruptly to be a shoulder and the one at 1730 cm^{-1} appreciably weakens, as in spectrum b of Figure 1. In this spectrum, instead, a broad absorption appears with a peak at about 2900 cm^{-1}, together with an absorption at about 2200 cm^{-1}. With further dehydration, the absorption at 3416 cm^{-1} weakens progressively to be not observed at all at the most dried, and the one at 1730 cm^{-1} becomes at last a shoulder. In contrast, the newly appearing absorptions become clearer and stronger with the progress of dehydration; that is, the absorption at about 2900 cm^{-1} becomes stronger and shifts down to show a strong absorption at 2741 cm^{-1} with a large absorption width, and the one at about 2200 cm^{-1} increases in intensity to become a clear absorption at 2203 cm^{-1}.

The characteristic feature of the spectral change of the Nafion membrane during dehydration is generally characterized as follows. Two absorptions weaken with the progress of dehydration, whereas other two absorptions intensify on the contrary. In addition, the spectral change has the following note-worthy feature. At the beginning of the measurement or when the Nafion membrane contains water possibly above a definite content, the measured spectrum does not pass through the isosbestic points, as spectrum a in Figure 1, but when the content of water is below the level, all of the spectra measured pass exactly through

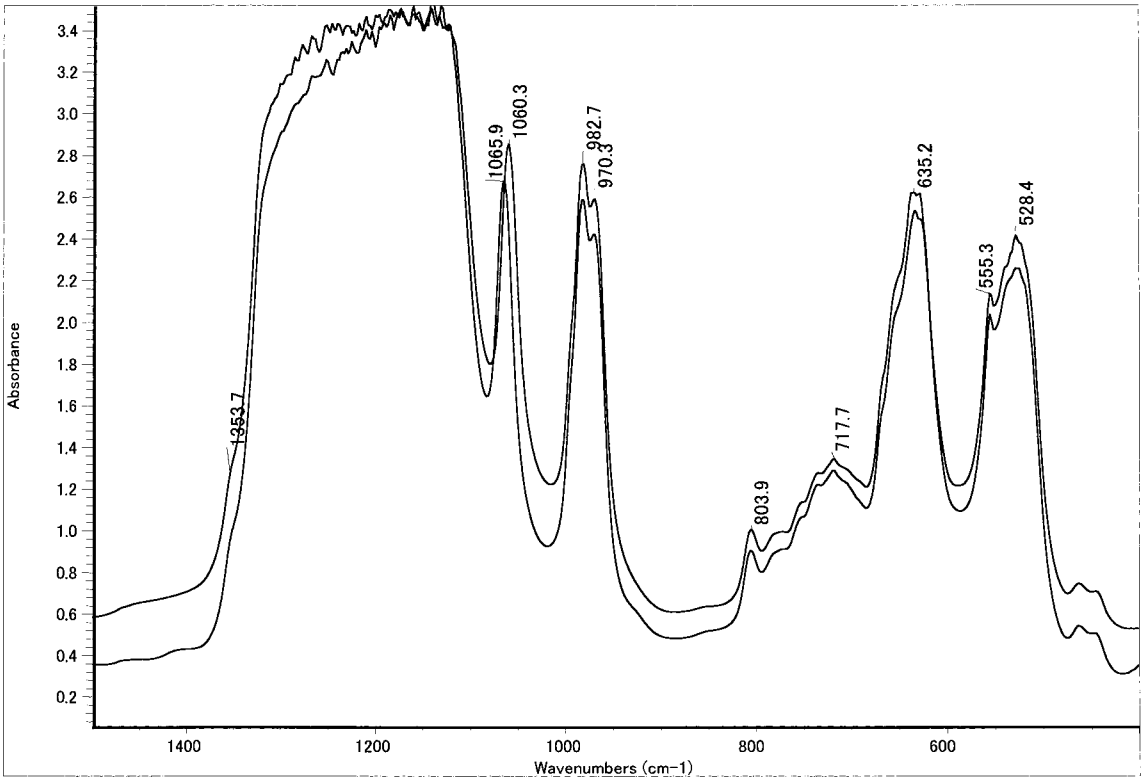

Figure 2. The upper (a) and lower (b) spectra are the 1500−400 cm^{-1} region of spectra b and i in Figure 1, respectively. The peak at 1065.9 cm^{-1}, which is over the other, is of spectrum b.

the two isosbestic points at 3027 cm^{-1} and 2043 cm^{-1}. This seems to indicate that there exists a critical content of water in the membrane, which determines whether a spectrum passes the isosbestic points or not.

It should be noted that the spectrum of the membrane does not show such significant changes in the 1500−400 cm^{-1} region by dehydration as in Figure 2, in which this region of spectra b and i of Figure 1 is shown. The two spectra were chosen because spectrum b of Figure 1 begins to pass the isosbestic points during dehydration, while spectrum i of Figure 1 is the one measured at the most dryness, and the difference between the two should be most significant among any two of all of the spectra, although the absorption in the 1300−1100 cm^{-1} region is saturated.

Here, let us consider the chemical change that causes the spectral changes observed in Figure 1. The spectral changes are considered to be caused by the release of water hydrated to the SO_3H group in the acid-type membrane, because the membrane of a salt-type does not show any complicated spectral changes at all, but only the absorptions due to water in the 3700−3500 cm^{-1} region and around 1630 cm^{-1} simply decrease in intensity with the progress of dehydration. The whole spectral changes following dehydration are not shown here, but only the spectrum of the sodium salt membrane, which is most dehydrated, is shown in Figure 3. It has weak absorptions at 3668 and 3524 cm^{-1} in the wavenumber region above 3000 cm^{-1} and at 1626 cm^{-1}. The former absorptions are assigned to OH stretching vibrations of water contained in the membrane, while the latter is assigned to the OH deformation. The absorption at 2366 cm^{-1} in Figure 3 is assigned to the combination of CF stretching vibrations at 1156 and 1212 cm^{-1}.[12] The absorptions at 2741 and 2203 cm^{-1} of the acid-type membrane, appearing most strongly in Figure 1, spectrum i, are not observed at all in the spectrum of Figure 3, suggesting that the absorptions are associated with the SO_3H group.

The observations above-mentioned suggest that the absorptions at 3416 and 1730 cm^{-1}, appearing most strongly in Figure 1, spectrum a, should be not of water itself but of such a chemical species derived from water as H_3O^+, which may decompose with the release of water to combine with coexisting RSO_3^- to produce RSO_3H with the progress of dehydration in the membrane. The absorptions at 2741 and 2203 cm^{-1}, which increase in intensity with dehydration for the acid form but do not appear at all for the sodium salt, are assigned to SO_3H. This assignment is reasonable in reference to a previous report.[13] From the above consideration, we have come to the idea that the key reaction concerned with the spectral changes in Figure 1 should be $H_3O^+ + RSO_3^- \rightarrow RSO_3H + H_2O$ (evaporating out). Then, the whole process that occurs with the evaporation of water contained in the membrane, should be given by the following stages from I to IV:

$$\underset{\text{I}}{AH_2O + BH_3O^+ + BRSO_3^- + CRSO_3H} \rightarrow \underset{\text{II}}{B_0H_3O^+ + B_0RSO_3^- + C_0RSO_3H} \rightarrow (B_0 - x)H_3O^+ + xH_2O\ (\text{evaporating out}) + \underset{\text{III}}{(B_0 - x)RSO_3^-} + (x + C_0)RSO_3H \rightarrow \underset{\text{IV}}{(B_0 + C_0)RSO_3H} \quad (1)$$

where B is the quantity in mole of RSO_3^- and H_3O^+ in equilibrium with that (C) of RSO_3H, as will be discussed below, and A mole of free H_2O in the membrane at the stage I, B_0 is similarly the quantity of RSO_3^- and H_3O^+ in equilibrium with that (C_0) of RSO_3H at the stage II when free water just evaporates out, and x is the quantity in mole of water at the stage III that evaporates out of the membrane after the stage II. During the evaporation of water, the membrane at the stage I passes through the stage II quickly to the stage III, where *an*

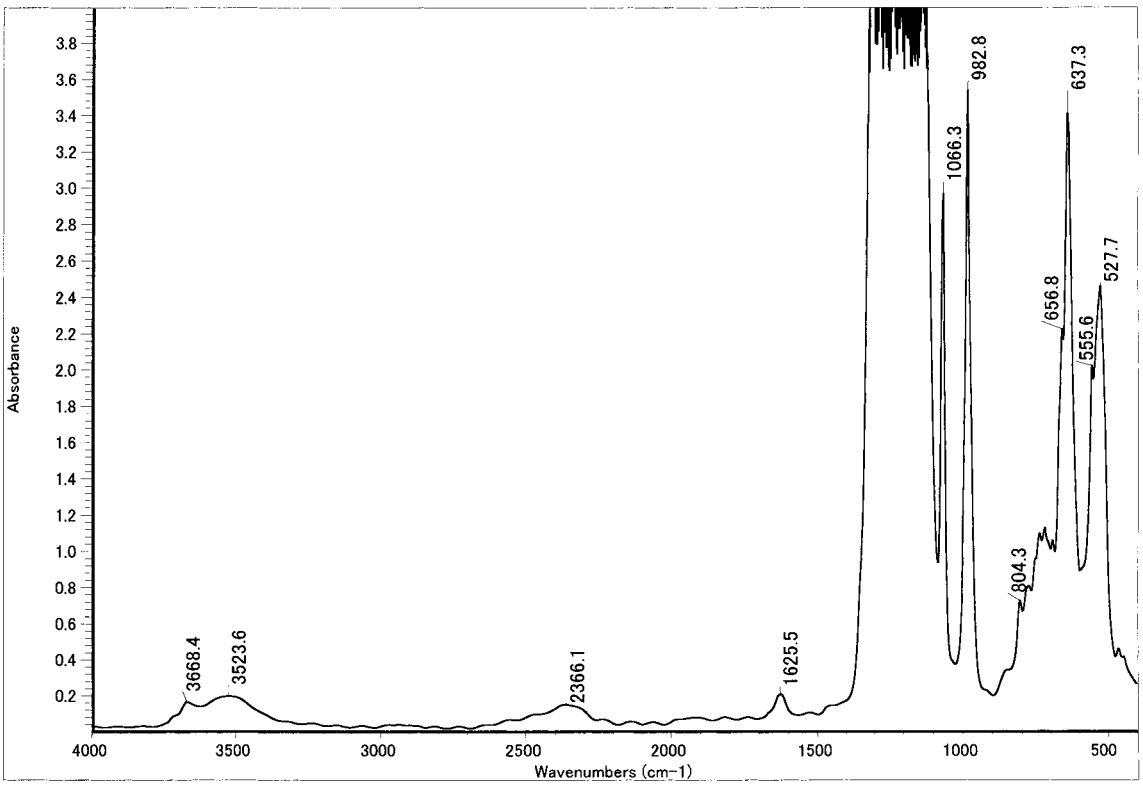

Figure 3. An FT-IR spectrum of a most dried Nafion112 membrane of the sodium salt type.

oxonium ion or H_3O^+ decomposes with the release of H_2O to give a proton or H^+, which combines with RSO_3^- to produce an equimolar SO_3H so that each spectrum measured at the stage passes the isosbestic points. At the last, when the membrane is completely dehydrated, it reaches the stage IV, where there exists the species RSO_3H only in the membrane.

Spectrum a of Figure 1, which does not pass through the isosbestic points, is of the stage I, where free H_2O coexists with H_3O^+. Spectrum b of Figure 1 begins to pass through the isosbestic points, and all of the subsequent spectra pass through the isosbestic points, the membrane showing the spectra being at the stage III. Spectrum i of Figure 1, which was measured after dehydration for 74 min after spectrum h of Figure 1, is only slightly different from this. Therefore, spectrum i of Figure 1 is treated as practically of RSO_3H, hereafter.

The chemical change given as the formulation 1 that appears in the acid-type Nafion membrane with the progress of dehydration was proposed on the basis of the absorptions concerned with OH stretching and deformation vibrations of H_2O, H_3O^+, and HO of SO_3H, which appear in the 4000−1500 cm^{-1} region. On the other hand, a spectral change may occur also with respect to the absorption of the S−O stretching absorption corresponding to the change from SO_3^- to SO_3H given in the above formulation. According to a previous report of infrared spectra of Nafion of the acid type,[5] an absorption of the S−O stretching is expected to appear at 920 cm^{-1}. In Figure 2, the absorption does not seem to appear with the production of SO_3H. The possible absorption was in more detail investigated by taking the difference (Figure 4) between the two spectra b and i of Figure 1, which correspond to the two spectra in Figure 2. In the difference spectrum (spectrum b − spectrum i), the absorptions due to H_3O^+, which decomposes with the progress of dehydration, should appear as plus peaks, whereas those due to SO_3H, which produces on the contrary, should appear as minus peaks. As expected, the absorptions due to H_3O^+ appear as plus peaks at 3420 and 1726 cm^{-1}, while those due to SO_3H do as minus peaks at 2665 and 2199 cm^{-1}. In Figure 4, any significant minus peak does not appear at all around 920 cm^{-1}, which can be assigned to the S−O stretching of SO_3H. The most conspicuous change by dehydration in the 1500−400 cm^{-1} region is a differential curve appearing in the 1070−1050 cm^{-1} region, which is caused by the peak shift from 1060 to 1066 cm^{-1} on dehydration as observed in Figure 2.

The absorption that was reported to be assigned to the S−O stretching absorption of the SO_3H group[5] was investigated for the published spectra of sulfonic acid compounds.[14,15] The spectrum of trifluoromethanesulfonic acid has the absorption of SO_3H in addition to the absorptions of H_3O^+,[14] indicating that the sample is a mixture of $CF_3SO_3^-H_3O^+$ and CF_3SO_3H. However, any absorption does not appear around 900 cm^{-1}. By contrast, a strong absorption appears at 900 cm^{-1} both for CH_3SO_3H and $CH_3CH_2SO_3H$.[15] This observation may suggest the possibility that the absorption at 900 cm^{-1} is of alkylsulfonic acid but not of perfluoroalkylsulfonic acid.

Although it was not possible to observe a significant spectral change except for the frequency shift of the absorption around 1060 cm^{-1} with respect to the S−O stretching absorption, the observed spectral changes in the 4000−1500 cm^{-1} region are in complete agreement with the formulation 1.

According to the formulation 1, the spectrum of H_3O^+ is separated by subtracting the spectrum of RSO_3H from any one at the stage III so as to cancel the absorption at 2741 cm^{-1}, because the coexisting RSO_3^- does not have significant absorptions above 1500 cm^{-1}. The spectrum of H_3O^+ was thus separated for spectra c and g of Figure 1, and the two spectra obtained are shown in Figure 5. They are essentially the same, although the concentration of H_3O^+ in the membrane is very different between them. There appear mainly two absorptions around 3300 cm^{-1} and at about 1720 cm^{-1}. The former has a large absorption width, showing two unseparated peaks at about 3370 and about 3120 cm^{-1}, which may be assigned to OH stretching vibrations of ν_3 and ν_1, respectively.[16] The one at

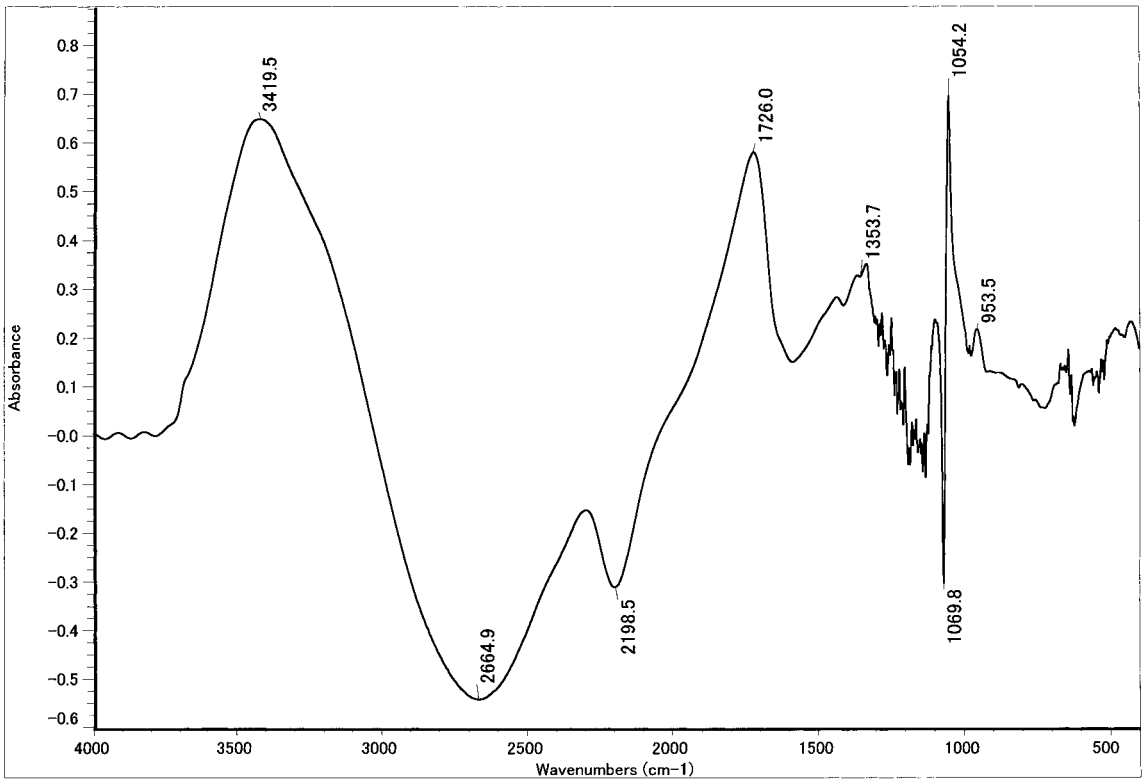

Figure 4. The difference spectrum (spectrum b − spectrum i of Figure 1). The frequencies of peaks, plus or minus, are not the same as those of SO_3H in Figure 1, spectrum i and of H_3O^+ in Figure 6, because this is a simple subtraction with the subtraction factor = 1.

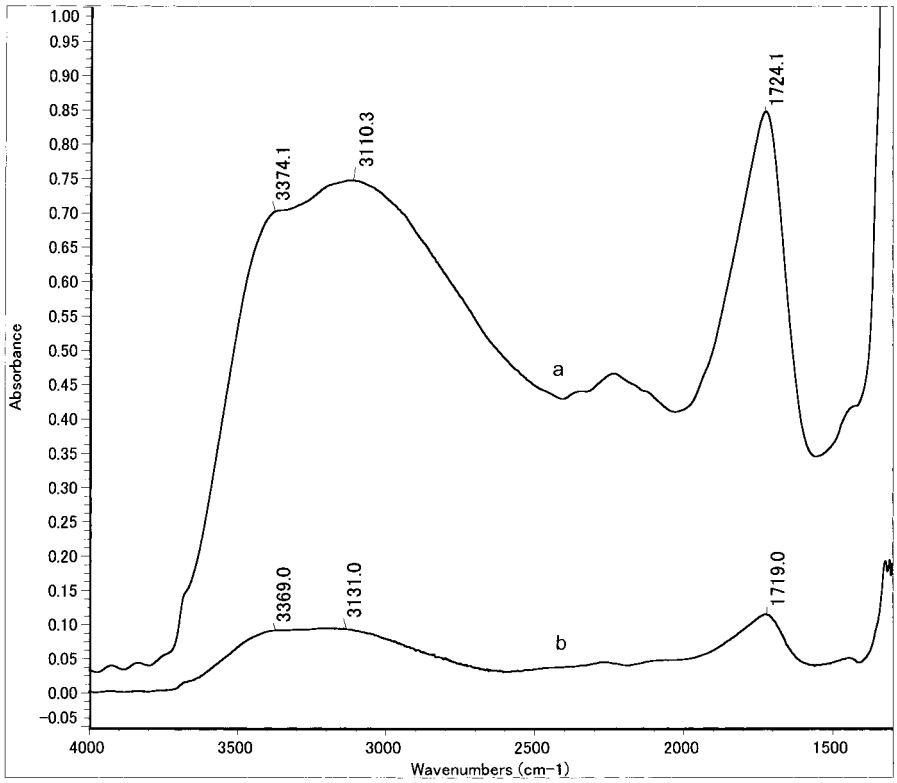

Figure 5. The spectrum of H_3O^+, separated for (a) spectrum c of Figure 1 and (b) spectrum g of Figure 1. The ordinate is the same for the two spectra.

1729 cm^{-1} is assigned to the OH deformation of ν_4.[16] There are some previous reports on the vibrational spectra of H_3O^+ as hydrates of such inorganic acids as perchloric acid, nitric acid, sulfuric acid, etc.[17,18] The feature of the infrared spectrum of H_3O^+ in Figure 5 is in good agreement with the Raman spectrum of $H_3O^+ClO_3^-$ in the crystalline state at −21 °C.[17]

It is interesting to compare the infrared spectra of H_2O and H_3O^+. In the stage I, H_2O coexists with H_3O^+, RSO_3H, and

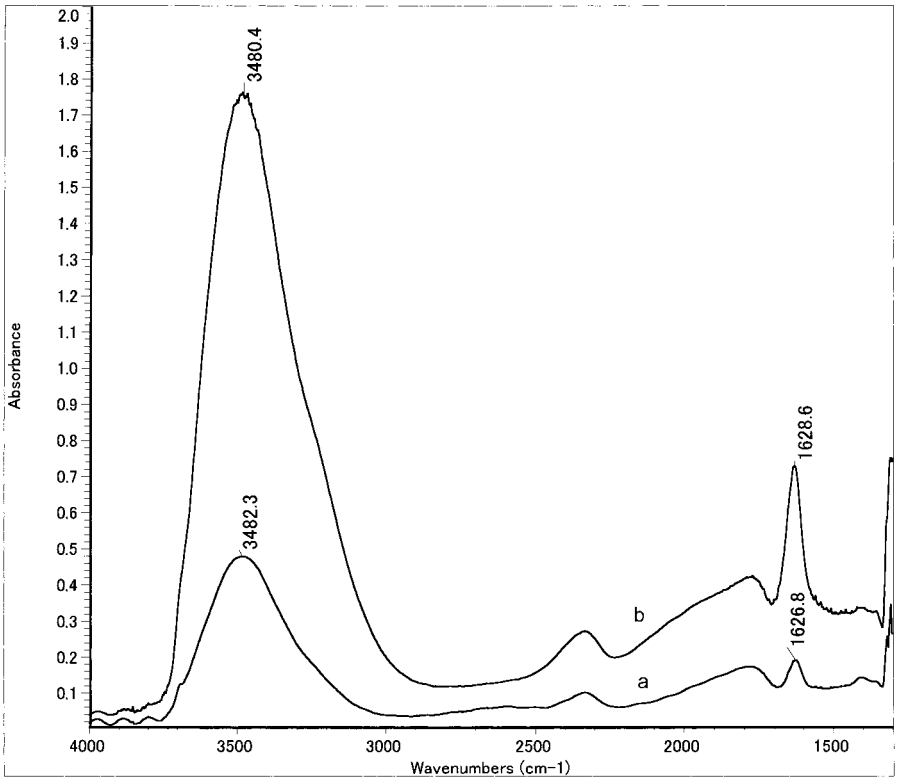

Figure 6. The spectrum of H_2O contained in the membrane at the stage I (a) separated for spectrum a of Figure 1, and (b) similarly separated for the membrane, which contains more water than that showing spectrum a of Figure 1. The ordinate is the same for the two spectra.

RSO_3^+ in the membrane. The spectrum of H_2O, then, is separated by independently subtracting the separated spectrum of H_3O^+ (Figure 5, spectrum a) and the spectrum of RSO_3H (Figure 1, spectrum i) with appropriate subtraction factors from spectrum a of Figure 1. The spectrum of water contained in the membrane thus separated is given in Figure 6a. In the spectrum, the absorptions at 3482 and 1627 cm^{-1} are assigned to the OH stretching and deformation vibrations, respectively, the ν_1 and ν_3 components of the former being nonseparable similarly as in liquid water. The spectrum of water in the Nafion membrane, similarly separated for the sample that, having been immersed in water, contains much more water is shown for comparison in Figure 6, spectrum b. This spectrum, which has much stronger intensities, is essentially the same as spectrum a in Figure 6 with respect to the frequencies and relative intensities of the two absorptions, confirming that they are truly characteristic of water coexisting with H_3O^+, RSO_3^-, and RSO_3H in the membrane. It is important to point out that the spectrum of water in the membrane is clearly different from that of H_3O^+ in Figure 5, with respect to the frequencies and shapes of the OH stretching and deformation absorptions and their relative intensities. In addition, the spectrum of water does not essentially change depending on the content in the membrane, coexisting with H_3O^+. Liquid water has absorptions at 4416 and 1648 cm^{-1} in the present measurement. It is well-known that as hydrogen bonding weakens, the OH stretching vibrations shift up, whereas the OH deformation shifts down, the magnitude of the shift being much larger for the former than for the latter.[19] The observed shifts of the OH absorptions of water in the membrane indicate that hydrogen bonding among water molecules is broken to some extent by coexisting H_3O^+. The observed IR spectrum of H_2O interacting with H_3O^+, which was for the first time separated to our knowledge, should be useful for understanding the interactions between them, for which the structure including H_3O^+ and H_2O in liquid was theoretically calculated.[20,21]

It is now possible to examine whether RSO_3H is completely dissociated into RSO_3^- and H_3O^+ when water contained in the membrane is equimolar to RSO_3H or more. This may be investigated for the state of the membrane that shows spectrum a of Figure 1, in which free water exists in excess over RSO_3H, as given by spectrum a of Figure 5. Subtraction of the spectrum of H_3O^+ in Figure 5, spectrum a, from spectrum a of Figure 1 leaves the absorptions due to RSO_3H or the spectrum i in Figure 1 to remain clearly. This indicates that RSO_3H is not completely dissociated into RSO_3^- and H_3O^+, even if there exists an equimolar water or more, but a fraction of RSO_3H exists without dissociation in equilibrium with H_2O, RSO_3^- and H_3O^+, in the membrane at the stage I, although we do not discuss quantitatively on the remaining amount of RSO_3H in the present study. This is the reason an amount of RSO_3H should be added at the stages I and II in the formulation 1.

Conclusion

In the present study, we have made it clear that water exists in equilibrium with H_3O^+, RSO_3^-, and RSO_3H in the Nafion membrane, when the water content is above a definite content, and that only H_3O^+ exists in equilibrium with RSO_3^- and RSO_3H without free water, when it is below the level. On the basis of the observation, it was possible to separate clear and distinctive infrared spectra of high quality, of H_3O^+ and of water coexisting with H_3O^+, spectroscopically demonstrating that the H_3O^+ ion can exist free from water in the Nafion membrane and that water coexisting with H_3O^+ is clearly different from liquid water. The H_3O^+ ion plays an important role in chemistry. On the basis of the present finding, it is possible to control the amount of water contained, coexisting with H_3O^+, in the

membrane, at any level from its upper limit determined by the solubility of water in the membrane at the stage I to zero at the stage III, under the controlled humidity of the surroundings. This makes it possible to study the chemical and physicochemical properties of H_3O^+ ions at the various concentrations. The present finding may contribute to a deeper understanding of the chemistry of H_3O^+.

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References and Notes

(1) The perfluoro polymeric part other than sulfonic acid of Nafion is denoted as R in the present paper.

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