

Hydration and Interfacial Water in Nafion Membrane Probed by Transmission Infrared Spectroscopy

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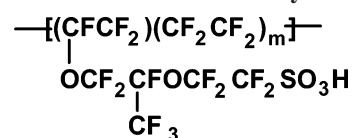
Infrared spectroscopy was applied to probe water inside pores and channels of Nafion membrane exchanged with either proton (H^+) or sodium ions (Na^+). Transmission measurements were performed on freestanding Nafion 112 ($\sim 50 \mu\text{m}$ thickness) in a cell that enabled adjustment of the relative humidity. Experiments that employed Na^+ -exchanged Nafion focused on relative humidity environments at or below about 32% generated through the use of humectants. Under these conditions, narrow features in the O–H stretching spectral region near $3650\text{--}3720 \text{ cm}^{-1}$, previously attributed to interfacial water, were detected and matched to bands in vibrational sum frequency (VSF) spectra of water/air, water/organic, and salt-solution/air interfaces. The features correspond to the stretching mode of the “free” OH group of water oriented with one hydrogen atom toward other water molecules and interacting through hydrogen bonding and the other straddling the interface extending into fluorocarbon-rich regions ($\sim 3668 \text{ cm}^{-1}$) or air-filled segments ($\sim 3700 \text{ cm}^{-1}$) in the membrane. For membrane exchanged with H^+ , $-\text{SO}_3^-$ groups were easily shifted to $-\text{SO}_3\text{H}$ as water was removed upon exposure to a few Torr of vacuum at 95°C . In contrast, residual water was retained by membrane exchanged with Na^+ after exposure to these conditions for up to 72 h. The permeation of methanol and acetone into Na^+ -exchanged Nafion 112 was also examined. The C–H and O–H stretching modes of methanol were perturbed in a manner that suggests the polymer disrupts hydrogen bonding interactions within the solvent, similar to the effect it exerts on pure water. For acetone, the C–H stretching modes were not shifted appreciably compared to those of the bulk liquid. However, the carbonyl band was affected, indicating the likely importance of dipolar interactions between solvent molecules and polar groups on the polymer. Control experiments performed with poly(hexafluoropropylene-*co*-tetrafluoroethylene) (FEP) membrane did not show evidence for water or methanol permeation, which demonstrates the critical role played by the ion-filled channels and pores in facilitating solvent transport within Nafion membrane.

Introduction

The perfluorosulfonated ion exchange material Nafion^{1,2} has played an important role in practical areas of electrochemistry, including fuel cells, water electrolyzers, chloralkali cells, and chemical sensors.^{1,3} Nafion contains a poly(tetrafluoroethylene) backbone and perfluoroether side chains that terminate in a sulfonate group.¹ A general structure is shown in Scheme 1. The performance of Nafion as an ion transport material is influenced by the interaction of water molecules with ion-exchange groups ($-\text{SO}_3^-$) on the polymer and free charge-compensating cations (e.g., H^+ , Na^+ , etc.) within the pores and channels of the polymer.^{2–5} Molecular level interactions that influence the state of water in Nafion materials have been investigated by spectroscopic techniques.¹ The sensitivity of infrared spectroscopy toward water has made it valuable for the study of hydration.^{6–18} Perturbations to the O–H stretching and H–O–H bending modes have been detected and ascribed to water molecules present in different environments inside Nafion, such as in nanometer-scale clusters,^{16,19} at polymer interfaces,^{7,9,16,19} and within proton solvent shells (i.e., $(\text{H}_2\text{O})_n\text{H}^+$, where n can vary from 1 to large values).^{11,14,18}

This paper presents results of infrared spectroscopy experiments that shed further light on properties of interfacial water within Nafion membrane. Transmission infrared measurements

SCHEME 1: Structure of Nafion Polymer



were performed on freestanding Nafion 112. A cell was used that enabled the humidity of the gas surrounding the membrane to be adjusted.^{11,14,17} The thickness of Nafion 112 is $\sim 50 \mu\text{m}$. Thus, the strong vibrational modes of the polymer backbone, which involve mainly $-\text{CF}_2$ and $-\text{SO}_3^-$ group motion, become saturated in transmission infrared measurements.^{11,15,16,18} However, the fundamental vibrational modes of Nafion are below 1500 cm^{-1} . The region above 1500 cm^{-1} is free of bands from the strong fundamental vibrational modes of the polymer, enabling the observation of features for permeating molecules (i.e., vapor of water and other types of solvents).^{7,9,11,14,16,17}

The work described herein focuses on perturbations to the O–H stretching modes of water in the spectral region between 3000 and 4000 cm^{-1} . In addition to the broad features typical of modes for bulk liquid water, also observed are sharper features in the range of $3650\text{--}3720 \text{ cm}^{-1}$ characteristic of the “free” OH stretching mode for interfacial water.^{7,9,16,20–22} Measurements were performed on Nafion membrane in H^+ - and Na^+ -exchanged forms in different hydration states at ambient temperature and pressure. Insights into the environment for water

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in Nafion membrane are gleaned through comparisons to vibrational sum frequency (VSF) spectroscopy studies of water/organic, water/air, and salt-solution/air interfaces.^{20–27} Spectra reveal effects of water associating with fluorocarbon-rich regions and other environments in the polymer. The permeation of methanol and acetone into Nafion was also probed, and parallel measurements with water, methanol, and acetone were performed on poly(hexafluoropropylene-*co*-tetrafluoroethylene) (FEP) membrane. It is shown that the porosity of Nafion imparted by phase separation and aggregation of the charged, polar $-\text{SO}_3^-$ groups facilitates the permeation of these solvents into the membrane.

Experimental Section

Nafion 112 membrane (30 cm \times 30 cm) was purchased from Ion Power Inc. (New Castle, DE). FEP membrane (50 μm thick) was obtained from American DuraFilm (Holliston, MA). The isotopically labeled compound D_2O (99.9% purity) was obtained from Cambridge Isotope Laboratories (Andover, MA). H_2SO_4 (99.999% purity), NaCl (99% purity), and LiCl (99% purity) were from Aldrich (Milwaukee, WI). $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (99.96% purity) was from Mallinckrodt, Inc. (St. Louis, MO). The H_2O_2 (3 vol % (v/v)) was from Aaron Industries, Inc. (Lynwood, CA). All aqueous solutions were prepared with deionized water (18 $\text{M}\Omega \cdot \text{cm}$) from a four-cartridge Nanopure Infinity System (Barnstead, Dubuque, IA).

Infrared spectra were recorded on a Mattson Instruments RS/1 Fourier transform infrared spectrometer system operating with a liquid nitrogen cooled, narrow-band mercury–cadmium telluride detector. Spectra were computed from the average of 128 interferograms measured at 2 cm^{-1} resolution and apodized with a triangular function. The sample cell was based on previously reported designs^{11,14} and constructed by modification of an infrared transmission cell (Demountable Liquid Cell, Aldrich). The windows employed were made of ZnSe (32 mm diameter by 3 mm thick). When mounted in the cell, the windows were held parallel and separated a distance of 1.0 cm by a pair of Kel-F spacers, which sandwiched the membrane. The spacers were machined to include a port for entry of a syringe needle (23 gauge) and a shallow well beneath the port to hold a solvent droplet. Prior to each experiment, the windows were polished with 0.05 μm alumina and then rinsed in deionized water followed by acetone and then brief sonication in deionized water. In a final step, the windows were further rinsed in deionized water and then set in an oven at 95 $^\circ\text{C}$ to dry. The spectrometer bench and sample compartment were purged continuously with dry air (Balston Inc., Haverhill, MA).

Samples of Nafion and FEP measuring approximately 1 cm \times 1 cm were cut and cleaned according to procedures described previously.⁴ The samples were boiled in 3% (v/v) H_2O_2 for 1 h followed by rinsing in boiling deionized water for 1 h. Afterward, samples were converted to either the H^+ or Na^+ form by boiling in 0.5 M H_2SO_4 or 0.1 M NaCl , respectively, for 1 h. As a final step, an ion exchanged membrane sample was rinsed in boiling deionized water for 1 h. Both the H^+ and Na^+ forms of the film were colorless and transparent to the eye. The surfaces of the sample were then dried in air and finally inserted into the infrared transmission cell and sandwiched between the Kel-F spacers. Additional drying steps were carried out using either a conventional oven or a vacuum oven (Napco, Waltham, MA), as indicated in the text and figure legends. The sample was placed in a desiccator to cool to ambient temperature after removal from the oven and just prior to infrared measurements.

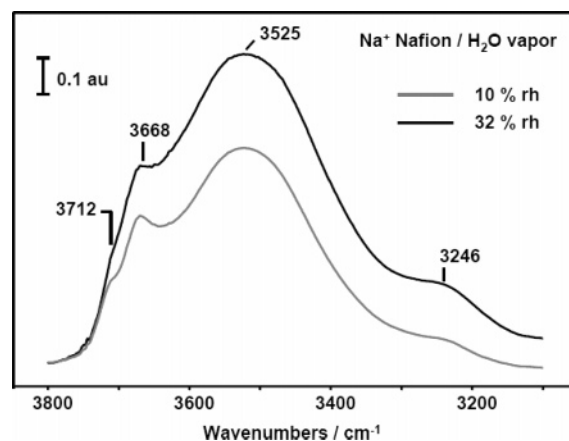


Figure 1. Transmission infrared spectra of Na^+ -exchanged Nafion 112 membrane equilibrated in air at room temperature above humectant that produces relative humidity values of approximately 10% or 32%, as indicated.

Spectra of bulk solvents were recorded either using a transmission infrared cell (Aldrich) equipped with ZnSe windows, or an attenuated total reflection (ATR) cell (Circle Cell, SpectraTech) with a ZnSe reflection element.

Results and Discussion

Figure 1 shows infrared spectra of a Na^+ -exchanged Nafion 112 membrane equilibrated in air above humectants that produce relative humidity values in the vicinity of 10% and 32% as indicated. The main features in the spectra are a broad band at 3525 cm^{-1} and two sharper bands near 3668 and 3712 cm^{-1} . Related spectra were reported by Falk and co-workers in early studies and discussed in terms of perturbations caused by interactions of water with the polymer and charge-compensating cations.^{7,9}

The band at 3525 cm^{-1} in Figure 1 is related to the broad feature peaked near 3400 cm^{-1} in transmission spectra of water.²⁸ Shifts of peaks in this region toward high energy indicate a disruption in hydrogen bonding among water molecules compared to bulk water.^{7,16,20,21,26} Falk ascribed features near 3525 cm^{-1} to modes of water molecules in the vicinity of Na^+ ions and $-\text{SO}_3^-$ sites.⁷

The sharper bands between 3650 and 3720 cm^{-1} in Figure 1 do not have counterparts in bulk water spectra, but analogous features have been detected in VSF measurements at water interfaces^{20–26,29} and in infrared studies of Nafion hydration.^{7,16} Falk suggested the peak near 3668 cm^{-1} arises from water molecules in an asymmetric environment extending one hydrogen atom toward fluorocarbon-rich regions of the polymer and the other toward nearby water molecules,⁷ or cation sites.⁹ Likewise, in VSF measurements at water/ CCl_4 ^{20,21,24} and water/hexane²¹ interfaces, an intense, sharp band at 3669 cm^{-1} has been assigned to stretching of the “free” OH group extending into the organic phase for water molecules that straddle the water/organic interface. The feature near 3712 cm^{-1} in Figure 1 correlates to Falk’s assignments for interfacial water oriented with both hydrogen atoms in the same phase.^{7,9} VSF measurements also show a prominent, sharp band near 3712 cm^{-1} in spectra of water/air and salt-solution/air interfaces.^{20–27,29} By analogy to the water/organic systems, this feature has been assigned to stretching motion of “free” OH groups extending into the vapor phase for molecules that bridge the interface.^{20–22,24,26,27,29} The assignment of bands near 3700 cm^{-1} in VSF spectra contrasts Falk’s explanation for the comparable bands that appear in infrared spectra of water in Nafion. The

differences can be reconciled to some extent by considering analyses that have been performed recently on VSF spectra of aqueous interfaces.^{20,21,23,24}

VSF spectra are complex and contain contributions from a number of vibrational modes that result from the wide range of orientations and environments possible for interfacial water.^{20,22–24,26} From a set of O–H stretching vibrational modes representing the important average configurations of interfacial water, VSF spectra were fit to corresponding line shape functions.^{20,21,23,24} It was determined that the population of water molecules situated with their oxygen atom toward bulk water and both hydrogen atoms in the nonaqueous environment contribute modes that have a relatively weak absorption intensity. However, these modes were shown to be capable of influencing the shape of the stronger bands arising from “free” OH groups and hydrogen bonded water through band overlap and effects of their phases during vibration. Comparing features in VSF spectra of water/CCl₄ and water/air interfaces, the intense bands near 3669 cm⁻¹ (water/CCl₄) and 3700 cm⁻¹ (water/air) were both assigned to modes of “free” OH groups with the shift in peak position reflecting the different dielectric properties of CCl₄ versus air.^{20,24} Results of the VSF studies suggest the two features in the region 3650–3720 cm⁻¹ in Figure 1 result from different populations of water in Nafion, with the lower energy band arising from “free” OH groups interacting with organic-rich areas of the polymer and the higher energy band reflecting “free” OH groups extending into dry regions containing atmospheric gases. Consistent with this assignment, Figure 1 shows that the 3712 cm⁻¹ feature does not grow as much as the other water bands as the relative humidity in the cell increases from 10% to 32%. This behavior is anticipated as the polymer takes on additional water and the water penetrates into dried areas.

Falk performed experiments with HOD to gain additional insights into the origin of the sharp water bands in the 3650–3720 cm⁻¹ region.^{7,9} In infrared spectra of Nafion membrane exposed to D₂O vapor containing a small amount of HOD, there was evidence for only a single feature with a peak in the range of 3660–3690 cm⁻¹ and the position depending upon the counteranion type and hydration level. The absence of a second band above 3700 cm⁻¹ in spectra of Nafion containing HOD strengthened arguments for the assignment of the ~3700 cm⁻¹ band in spectra of H₂O in Nafion to a mode of water in a symmetric coordination environment, such as oriented with its oxygen atom in water and both hydrogen atoms interacting with the polymer.^{7,9} Falk noted that this symmetric configuration should produce a second O–H stretching mode with energy expected near 3600 cm⁻¹.⁷ However, weak bands near 3600 cm⁻¹ can easily be obscured by the strong and broad hydrogen bonded water features in the region.^{7,9}

Experimental VSF spectra for the water/air interface show that in progressing from H₂O to small HOD quantities in D₂O the “free” OH band broadens extensively.²⁴ From line width considerations, it may be difficult in HOD experiments to resolve “free” OH bands across the 3650–3720 cm⁻¹ region associated with interfacial water in different types of environments. The HOD measurements undertaken by Falk and co-workers employed a dispersive spectrometer, and the resolution was not specified.^{7,9} We are currently investigating HOD permeation into Nafion using a Fourier transform infrared spectrometer at resolution near 1 cm⁻¹ to determine if there is evidence for additional environments.

The interfacial water features near 3650–3720 cm⁻¹ discussed above are prominent in infrared spectra of Nafion exchanged

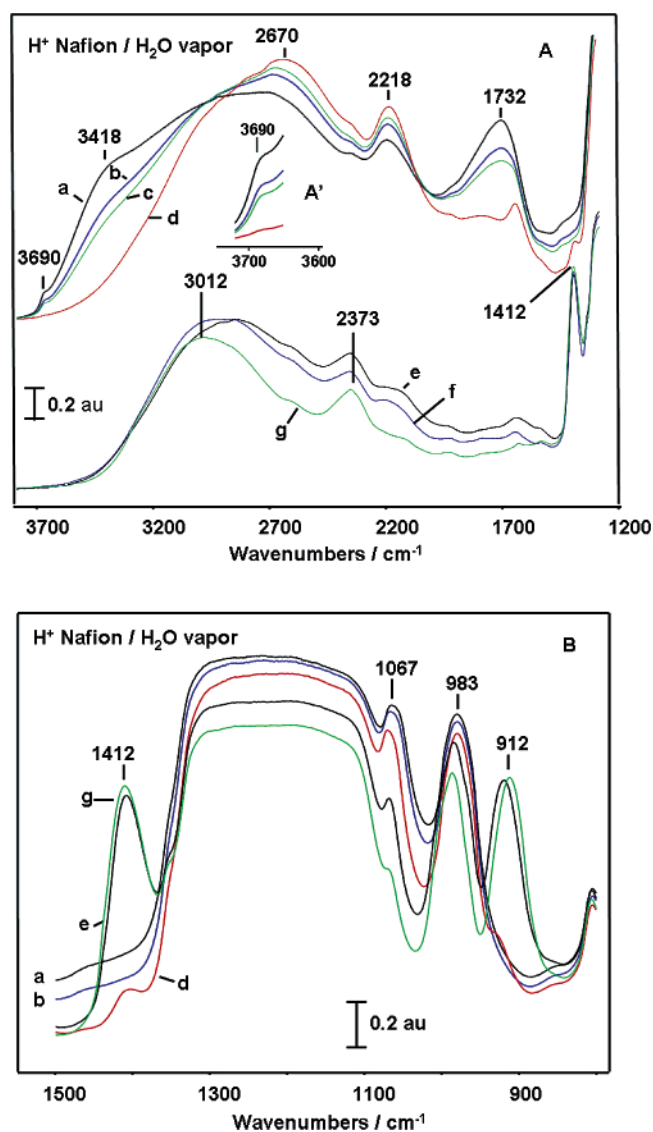


Figure 2. Transmission infrared spectra of H⁺-exchanged Nafion 112 membrane in air at room temperature during dehydration. The high-frequency region (A) and low-frequency region (B) are shown expanded. After washing, the membrane was initially exposed to 95 °C and ambient pressure for 10 min and subsequently treated according to the following sequential steps: held in dry air at ambient temperature for (a) 10 min, (b) 3.5 h, and (c) 5.5 h; (d) placed under a few Torr of vacuum at 65 °C for 1 h followed by dry air at ambient temperature for 5.5 h; (e) placed under a few Torr of vacuum at 95 °C for 1 h followed by dry air at ambient temperature for 15 min; (f) placed under a few Torr of vacuum at 95 °C for 25 h followed by dry air at ambient temperature for 15 min; (g) placed under a few Torr of vacuum at 95 °C for 72 h followed by dry air at ambient temperature for 15 min. In (A), the inset (A') is an enlargement of the region near 3690 cm⁻¹ for spectra a–d (top–bottom).

with Na⁺ and other metal cations.^{7,9,15,16} For membrane in H⁺ form, only a single band in the vicinity of 3690 cm⁻¹ has typically been observed.^{11,15} An example is shown in Figure 2A. The upper set of spectra in Figure 2A report properties of H⁺-exchanged Nafion 112 during dehydration steps starting from a film that has been washed (see Experimental Section) and then immediately oven dried at 95 °C for 10 min to remove residual water (spectrum a). In spectra labeled “a”–“c”, a weak band that can be ascribed to interfacial water is present at 3690 cm⁻¹. The interfacial water region is expanded in the inset (A') to Figure 2A. The marked differences in the interfacial water features between Nafion in the Na⁺ and H⁺ forms may be a

result of the behavior of H_3O^+ relative to Na^+ at interfaces.²⁷ Mucha and co-workers showed that hydronium ions have a tendency to partition to the water/air interface and displace water, while small alkali metal cations are repelled from the interface and favor positions just below the interfacial water layer.²⁷ In the strongly acidic environment inside H^+ -exchanged Nafion, the number density of “free” OH groups at water/air interfaces is likely small. The composition may be such that configurations contributing to the 3712 cm^{-1} band are no longer present. Consistent with this idea, the sharp “free” OH band near 3712 cm^{-1} decreases as the solution pH becomes lower in VSF spectra of salt-solution/air interfaces.²⁷ Since Nafion can easily be present in states with only a few water molecules per H^+ ,^{11,14,15} “free” OH groups produced will be those derived from $(\text{H}_2\text{O})_n\text{H}^+$ clusters. The 3690 cm^{-1} band, then, can possibly be ascribed to “free” OH groups of $(\text{H}_2\text{O})_n\text{H}^+$ clusters, possibly at polymer–water interfaces, although the assignment is not definitive.

In spectrum a in Figure 2A, a shoulder is prominent near 3418 cm^{-1} to the high-energy side of a broad peak that extends from 2300 to 3750 cm^{-1} . The 3418 cm^{-1} shoulder lies close to the position expected for bulk water (3400 cm^{-1}).²⁸ Intensity in this shoulder region diminishes (spectra a–c) as water is removed from the film during exposure to the dry air purge in the spectrometer. The loss is offset by growth in a feature near 2670 cm^{-1} . Upon further drying by placing the membrane under a few Torr of vacuum at $65\text{ }^\circ\text{C}$ (spectrum d), peak intensity in the region shifts to 2670 cm^{-1} and the interfacial water band at 3690 cm^{-1} is no longer evident.

The general behavior in the spectra of H^+ -exchanged Nafion during water loss has been discussed in terms of $(\text{H}_2\text{O})_n\text{H}^+$ structures transitioning from large n to $n \approx 1$ as dehydration progresses.^{11,14,15} Buzzoni has described the complicated nature of vibrational modes for aqueous acid solutions¹¹ and ascribed a broad band at 2750 cm^{-1} to an O–H stretching mode of H_3O^+ interacting with $-\text{SO}_3^-$ groups. The 1732 cm^{-1} band in Figure 2A has also been discussed previously as arising from bending modes of $(\text{H}_2\text{O})_n\text{H}^+$ species.^{11,14,15} Between acquisition of spectrum d and spectrum e in Figure 2, the membrane was again placed under a few Torr of vacuum, this time at $95\text{ }^\circ\text{C}$. At the higher temperature, additional water was expelled. The spectrum recorded afterward (Figure 2Ae) shows several changes. The broad O–H stretching feature has shifted toward 3012 cm^{-1} , the 1732 cm^{-1} band is no longer present, and a prominent new feature close to 1412 cm^{-1} is apparent. Bands at 3012 and 1412 cm^{-1} are known to be characteristic of $-\text{SO}_3\text{H}$ groups in Nafion along with a band at 912 cm^{-1} (Figure 2B) due to the S–OH stretching mode.^{11,14,15} Thus, the spectrum indicates that placing the H^+ -exchanged membrane under a few Torr of vacuum at $95\text{ }^\circ\text{C}$ for 1 h results in water loss sufficient to shift the ionized sulfonate groups into the $-\text{SO}_3\text{H}$ form. Spectra f and g in Figure 2A show that performing the treatment over longer periods leads to further water loss as evidenced by the appearance of a more well-defined band at 3012 cm^{-1} and flattening of the region around 1732 cm^{-1} .

In addition to the 912 cm^{-1} band for the $-\text{SO}_3\text{H}$ group, the set of lower energy mid-infrared spectra in Figure 2B include other modes of the Nafion polymer. The band near 1067 cm^{-1} arises from symmetric stretching of the $-\text{SO}_3^-$ group.^{6,10,11,14,17} Its intensity diminishes in parallel with the growth of bands for $-\text{SO}_3\text{H}$.^{11,14} The band in the region at 983 cm^{-1} has been ascribed to modes of C–O–C groups on the polymer side chains.^{8,10,13,17,18} The band does not show strong shifts in position or intensity during changes in hydration state. It is difficult to

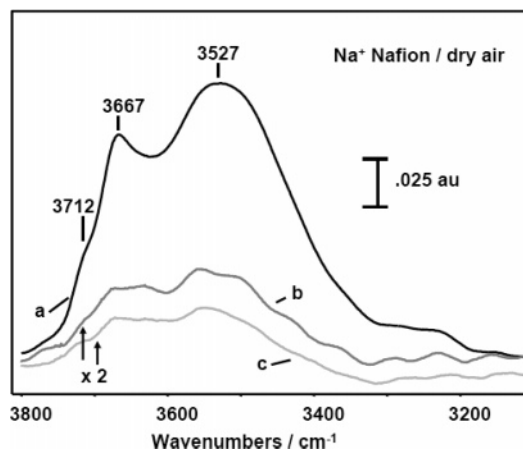


Figure 3. Transmission infrared spectra of Na^+ -exchanged Nafion 112 membrane after drying in (a) air at $95\text{ }^\circ\text{C}$ and under a few Torr of vacuum at $95\text{ }^\circ\text{C}$ for (b) 1 h and (c) 72 h.

quantitatively interpret the small changes that are present, since the membrane shows some deformation due to shrinkage during dehydration.

The spectra in Figure 2 and related literature reports^{11,14} indicate that nearly complete removal of water from H^+ -exchanged Nafion can be achieved by application of a few Torr of vacuum and temperatures close to $100\text{ }^\circ\text{C}$. Similar behavior does not occur as readily for Na^+ -exchanged Nafion, likely because water provides stabilization for the charged ionic species in the membrane.^{6,11,15,16} Figure 3 shows spectra of Na^+ -exchanged Nafion recorded following different drying procedures and times. After drying at ambient pressure and $95\text{ }^\circ\text{C}$ (Figure 3a), bands of the retained water are apparent. The intensity at 3527 cm^{-1} is about 4 times smaller than that observed for the membrane equilibrated in an atmosphere of approximately 10% relative humidity (Figure 1). In addition, features for the two different interfacial water environments are prominent. The band ascribed to water–fluoropolymer interactions peaks at 3667 cm^{-1} , and its intensity is almost equal to the feature for the O–H stretching mode of weakly hydrogen bonded water at 3527 cm^{-1} in the spectrum. The relative intensities of the interfacial versus weakly hydrogen bonded water bands in Figures 1 and 3 indicate that the water clusters being detected in spectrum a of Figure 3 have the higher surface-to-volume ratio. Placing the membrane under a few Torr of vacuum at $95\text{ }^\circ\text{C}$ for 1 h lowers the water content further (Figure 3b). The combination of elevated temperature and low pressure likely opens pathways for the release of water vapor which had become trapped as the membrane dropped below the percolation threshold during dehydration.¹⁶ Spectrum c in Figure 3 was recorded after exposure of the membrane to vacuum and high temperatures for 3 days. The water content is not changed considerably in comparison to the initial evacuation period. Also worth mentioning is that the band for the symmetric stretching mode of the $-\text{SO}_3^-$ group shifts from 1068 cm^{-1} in spectrum a of Figure 3 (data not shown) to 1075 cm^{-1} in spectrum c, consistent with the strong upshift in this mode that is known to occur upon dehydrating the ion-rich regions of Nafion exchanged with metal cations.⁶

Since the rapid diffusion of methanol in Nafion limits the use of Nafion as an ion transport medium in direct methanol fuel cells,^{2,30,31} we examined methanol permeation and its effect on the physical environment for water in the membrane. Figure 4A expands the O–H stretching region for spectra recorded with a Nafion 112 membrane above LiCl-saturated H_2O containing 10% (v/v) methanol. LiCl-saturated solution was used

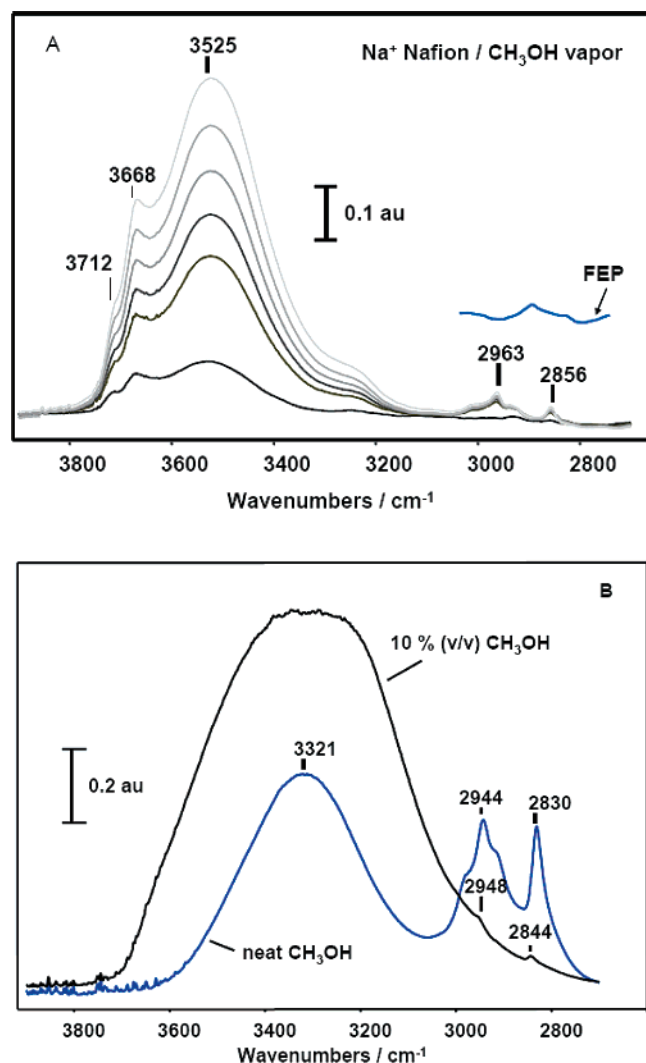


Figure 4. (A) Transmission infrared spectra of Na⁺-exchanged Nafion 112 membrane at ambient temperature after drying in air at 95 °C (bottom) and following subsequent exposure to atmosphere above LiCl-saturated H₂O containing 10% methanol for 10 min, 20 min, 30 min, 1 h, and 3 h (in order from the next to bottom spectrum to the top spectrum). The inset spectrum was recorded with FEP membrane following 3 h exposure to the solvent system. (B) Infrared spectra of neat methanol and a solution of 10% (v/v) methanol in water recorded using ATR sampling.

to reduce the water and methanol partial pressures in the vapor compared to the neat solvent mixture and thereby keep the spectral band intensities in a linear response range. In Figure 4A, bands at 2856 and 2963 cm⁻¹ correspond to stretching modes of the -CH₃ group for methanol.³² The remaining bands are similar to those of water in Figure 1. The bottom spectrum in Figure 4A reports on the water present in the membrane prior to addition of methanol to the cell. Following exposure to methanol solution, bands for both water and the -CH₃ group appear and grow in intensity over the 3 h measurement period. Stronger intensity changes are observed for the water bands, which over the course of the experiment reach intensities similar to those in Figure 1 for Nafion in a 10% relative humidity environment.

The positions of the bands for the -CH₃ group stretching modes in Figure 4A are shifted toward higher energy by ~20 cm⁻¹ compared to neat methanol and methanol at 10% (v/v) in water (Figure 4B).¹¹ Buzzoni and co-workers¹¹ used infrared spectroscopy to probe methanol in Nafion and detected perturbations in the methanol vibrational bands. However, the focus

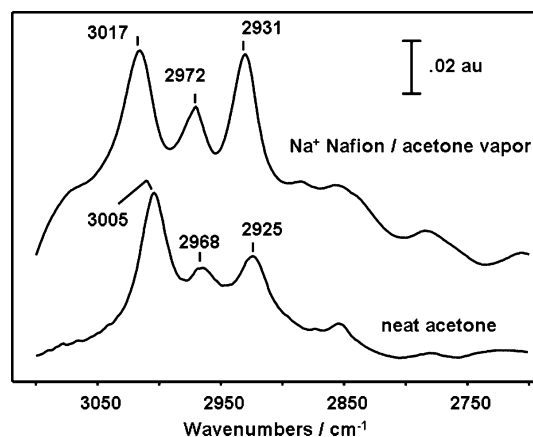


Figure 5. (top) Transmission infrared spectra of Na⁺-exchanged Nafion 112 membrane at ambient temperature after drying in air at 95 °C and following subsequent exposure to atmosphere above LiCl-saturated acetone. (bottom) Transmission infrared spectrum of neat acetone.

of the study was on the tendency of CH₃OH₂⁺ to form within H⁺-exchanged membrane. The band shifts observed in Figure 4A result in part from the broadness of the O-H stretching features of water. Figure 4B shows that the 2844 and 2948 cm⁻¹ peaks for methanol in 10% (v/v) solution coincide with the tail of the O-H stretching feature and appear at slightly higher energies than their counterparts in the spectrum of neat methanol. However, the major contributions are likely the disruption of hydrogen bonding and interfacial forces, both of which result from interaction of the solvents with Nafion. It is notable that the ratio of intensity at 3525 cm⁻¹ relative to 3668 cm⁻¹ (*I*₃₅₂₅/*I*₃₆₆₈) is somewhat larger in Figure 4 than in Figure 1, suggesting that methanol may displace some of the interfacial water. The importance of hydrogen bonding in methanol solutions has been discussed recently, and similar blue shifts with increasing water content have been observed in connection with VSF studies.³²

The bands for -CH₃ group modes in Figure 4A are better defined than those in the spectrum of the 10% (v/v) methanol solution (Figure 4B). The methanol:water composition within Nafion is expected to be the same as in the contacting vapor,^{30,31} which is likely enriched in methanol somewhat compared to the solution, in accordance with Henry's law. However, a more significant factor is probably the large shift in the broad O-H stretching band from ~3320 cm⁻¹ to near 3525 cm⁻¹ as hydrogen bonding forces within assemblies of solvent molecules in Nafion become weakened, opening the region below 3100 cm⁻¹ for observation of -CH₃ stretching modes. To probe these hydrogen bonding interactions further, the permeation of acetone into Nafion was examined. Although the carbonyl stretching mode near 1710 cm⁻¹ was shifted to 1725 cm⁻¹ for acetone in Nafion, there was much less effect on the -CH₃ modes compared to liquid acetone. Figure 5 shows that the largest change in prominent -CH₃ stretching modes is an upshift of about 12 cm⁻¹ for the 3005 cm⁻¹ band in neat acetone. The results likely reflect the loss of hydrogen bonding capabilities in going from methanol to acetone, yet with the possibility for favorable interaction between the polar carbonyl group and charged regions of the polymer.

Figure 4A includes a segment of a spectrum recorded following 3 h exposure of an FEP membrane (~50 μm thickness) to LiCl-saturated H₂O containing 10% methanol. Any methanol present in the fluoropolymer membrane is below the detection limit of the infrared experiment. In separate experiments, the permeation of water vapor into FEP was probed. As

expected, the fluoropolymer membrane resisted water incorporation. The lack of detectable quantities of water and methanol in the FEP membrane examined indicates that these molecules are transported within Nafion through the ion-rich channels and pores.

Conclusions

Transmission infrared spectroscopy provides a simple means for probing the permeation of solvent vapor into Nafion membrane and reveals insights into solvent structure, including polymer–solvent interactions. Spectra of Na⁺-exchanged Nafion 112 in atmospheres up to 32% relative humidity display narrow features in the O–H stretching region that can be ascribed to interfacial water inside the polymer. A band near 3670 cm^{−1} previously assigned to stretching of the “free” OH group of water interacting with fluorocarbon-rich regions of Nafion coincides with VSF spectra of water/CCl₄ and water/hexane interfaces. A second band near 3712 cm^{−1} correlates to the same mode in VSF spectra of water/air and water/salt-solution interfaces and is thus assigned to water molecules straddling the interface between condensed droplets inside nanoscale channels of Na⁺-exchanged Nafion and dry, air-filled regions in the polymer. In H⁺-exchanged Nafion, spectra are dominated by features of (H₂O)_nH⁺ clusters. Under a few Torr of vacuum and temperatures near 95 °C, −SO₃[−] groups shift to −SO₃H form, and it appears that complete removal of water from the membrane is possible. In contrast, water, which provides stabilization of the Na⁺ and −SO₃[−] groups, is more difficult to remove and is retained under the same conditions by Na⁺-exchanged membrane. Similar to water, hydrogen bonding among methanol molecules in Na⁺-exchanged Nafion is disrupted relative to the bulk liquid. Acetone also showed some evidence of dipolar interaction with the polymer, although the spectral perturbations were not as great as for methanol. Parallel measurements of solvent permeation into FEP membrane confirmed the importance of the pore and channel structure within Nafion in enabling transport of solvent.

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References and Notes

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