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Effect of Water on Internal Aggregate Structure in Zinc-Neutralized Ionomers

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ABSTRACT: The effect of water on zinc-neutralized ethylene−methacrylic acid (E−MAA) ionomers and sulfonated polystyrene (SPS) ionomers was studied. The change in weight after soaking in water was quantified as a function of zinc content and correlated to changes in spectra from zinc-edge extended X-ray absorption fine structure spectroscopy (EXAFS). EXAFS patterns for the fully dried ionomers were characteristic of zinc surrounded by four oxygen atoms. E−MAA ionomers absorbed much less water per zinc atom than SPS ionomers. Addition of water changed the EXAFS pattern in E−MAA ionomers, but the pattern was still characteristic of zinc coordinated to four oxygen atoms. This change was consistent with water replacing chelating carboxylate anions coordinated to zinc at the edges of aggregates or coordinated to isolated zinc ions. A new interpretation of the $\nu_a(COO^-)$ infrared vibration was developed from this work. In SPS, addition of water caused zinc to become 6-fold coordinated to oxygen, which is suggestive of zinc totally solvated by water.

Introduction

This paper is the sixth in a series exploring the arrangement of atoms in zinc-neutralized ionomers using extended X-ray absorption fine structure (EXAFS) spectroscopy.[1−5] In the first two papers, it was shown that the EXAFS patterns of well-dried zinc sulfonated polystyrene ionomers were consistent with a structure originally proposed by Ding et al.[6] In this structure, zinc is tetrahedrally coordinated to four oxygen atoms from four different sulfonate groups as shown in Figure 1. The sulfonate anions are bidentate and coordinated to two different zinc atoms while the third oxygen atom does not coordinate to zinc. In well-dried E−MAA ionomers,[3] zinc atoms are 4-fold coordinated to oxygen from four different carboxylate groups as represented by Figure 2. The arrangement of atoms in the aggregate very closely resembles the arrangement of atoms in monoclinic anhydrous zinc acetate.

This study examines the effect of water on the local aggregate structure in zinc-neutralized carboxylate and sulfonate ionomers. Water and other plasticizers can have a significant impact on the properties of ionomers. Two categories of small molecules are soluble in ionomers: those that significantly reduce the melt viscosity and those that do not. The latter are typically aliphatic molecules that act as plasticizers for the parent un-ionized polymer; however, in ionomers these types of molecules do not significantly reduce the melt viscosity but do significantly lower the glass transition temperature.

The other type of soluble small molecule is typically not soluble in the nonionic precursor but reduces the melt viscosity significantly in the ionomer, in some cases orders of magnitude. This type of molecule is usually polar and is believed to disrupt the aggregate structure. The experimental evidence for this explanation is not overwhelming, although an alternative explanation is difficult to hypothesize. Small-angle X-ray scattering (SAXS) patterns have shown different behavior depending on the plasticizer. If plasticizer were causing the aggregates to break up and the ionic groups to disperse uniformly in the polymer matrix, the ionomer SAXS peak should disappear. Methanol reduces the intensity of the ionomer peak in sulfonated polystyrene and shifts the peak toward lower angle (i.e., increased distance between scattering entities). In fully neutralized man-

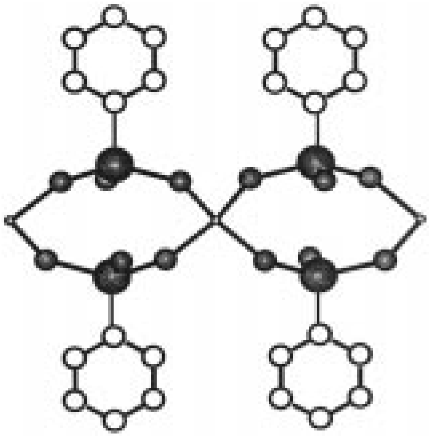

Figure 1. Schematic of proposed structure for dry zinc sulfonated polystyrene ionomers. Small filled circles represent zinc, larger filled circles represent oxygen, largest filled circles represent sulfur, and open circles represent carbon. Modeled after diagram appearing in ref 1.

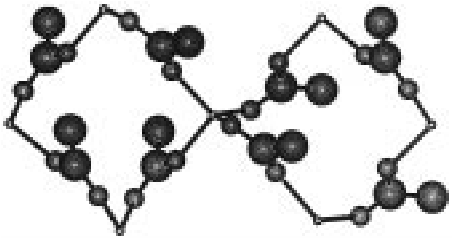

Figure 2. Schematic of proposed structure for dry zinc ethylene−methacrylic ionomers. Same symbols as in Figure 1, except largest filled circles represent carbon. Modeled after diagram appearing in ref 3.

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ganese sulfonated polystyrene with 1.65 mol % sulfonate groups, addition of methanol leads to the disappearance of the SAXS peak entirely.[7] Glycerol[7] and water[8] cause the same shift toward lower angle but also cause an increase in scattering intensity. If the polar molecules are preferentially absorbed by the aggregates, the opposing behavior of methanol and glycerol is simple to explain on the basis of the electron densities of methanol (268 e^-/nm^3) and glycerol (412 e^-/nm^3) compared to the electron density of polystyrene (340 e^-/nm^3). However, the effect of water is more difficult to explain since water's electron density is slightly lower (334 e^-/nm^3) than polystyrene's electron density. Further, electron spin resonance (ESR) studies of the manganese-neutralized materials indicated that manganese ions are separated by less than roughly 1 nm before and after glycerol addition; hence, manganese ions are still aggregated even after glycerol addition.

The effect of water and other plasticizers on the EXAFS pattern of ionomers has also been previously investigated. In these studies, the arrangement of atoms in the well-dried material was not as well understood as in this current work, and hence the conclusions were not as quantitative. Still, qualitative and semiquantitative information about the effect of water on ionomers is available. In zinc sulfonated polystyrene ionomers,[9] the addition of water decreased the height of the peak due to backscattering from the first coordination shell and shifted this peak toward higher R_F, which the authors interpreted as a shift in coordination number from 4 to 5. In fact, the decrease in height suggests a combination of 4-fold and 6-fold oxygen coordination environments, rather than a single 5-fold coordination environment. The addition of glycerol caused a shift from 4-fold to 6-fold coordination, although again the authors did not interpret the environment at an intermediate level of glycerol as being from a combination of 4-fold and 6-fold coordination. For nickel sulfonated and carboxylated polyurethane ionomers, the changes upon water addition were qualitatively different.[10] In the former, water absorption did not change the first shell environment significantly, while in the second case the number of oxygen atoms in the first shell increased significantly.

Highly swollen perfluorinated sulfonate ionomers have significant commercial importance, and hence the effect of water on the morphology and properties of these materials has been studied using EXAFS. In zinc-neutralized systems, oxygen coordination numbers changed from 4 to 6 as the water content changes from 0.4 to 18%. However, perfluorinated materials absorb tens of percent of water; hence, it is not clear that the significant changes are necessarily relevant for the types of systems studied in this paper.

Infrared spectroscopy has been used to examine the effect of water on local molecular environment in zinc-neutralized E−MAA ionomers. Infrared spectroscopy in the mid-IR region has been used to examine the antisymmetric $v_a(COO^-)$ stretch which is affected by the introduction of zinc into E−MAA copolymers. A study by Painter and Coleman[11] in a fully neutralized material attributed the band at 1585 cm^{-1} to tetracoordinated zinc. After the addition of water to a fully neutralized material, this band broadened slightly. A second study[12] on partially neutralized, nominally dry materials involving heating and cooling found three environments for dry zinc atoms: a tetracoordinated zinc (1585 cm^{-1}), a hexacoordinated zinc (1539 and 1560 cm^{-1}), and acid salts (1625 cm^{-1}). The acid salt structure occurred only when the temperature was raised to 100 °C. A later paper by a different author[13] showed that the ratios of absorption intensities for the bands at 1539, 1560, and 1625 cm^{-1} were identical at different water contents for an ionomer neutralized to approximately 50% of stoichiometric and hence concluded that all three bands were due to the same coordination structure in conflict with the Painter and Coleman paper.

The later paper also contained calculations for the number of water molecules per zinc atom by assuming that the band at 1585 cm^{-1} was from zinc atoms coordinated to water and the triplet at 1539, 1560, and 1625 cm^{-1} was from dry zinc atoms. By using the known amounts of water added, the author used this analysis to show that the nominally dried sample (50 °C, vacuum oven) still contained roughly one molecule of water per six zinc atoms, while the wet sample contained approximately three molecules of water per six zinc atoms.

This introduction described a number of investigations on the effect of water and other polar plasticizers on the local structure of ionomers. The study described in this paper differs significantly from previous studies because this study identifies precisely where in the aggregate water molecules are found.

Experimental Section

E−MAA ionomers were graciously supplied by DuPont Inc. in pelletized form by DuPont. Unless otherwise noted, the methacrylic acid content was 3.9 mol %. The zinc content of these partially neutralized materials was determined using electron microprobe analysis (EMPA), which had an error of approximately 5% based on duplicate measurements. To ensure the accuracy of EMPA measurements, one sample was also measured using inductively coupled plasma by Galbraith Labs. The results from the two methods were identical within the respective error of the measurements. A few appropriately sized samples with specific water contents were provided by DuPont in sealed bags for EXAFS analysis. For these samples, water content was determined by Karl Fischer analysis.

Polystyrene was sulfonated using the method of Lundberg et al.[14] Details of the sulfonation method are given in a previous publication.[15] The 3.4 and 5.7 mol % sulfonate substitution levels were synthesized. The acid form was dissolved in a 90/10 v/v mixture of toluene/methanol and neutralized with a stoichiometric amount of zinc acetate dihydrate to produce fully neutralized zinc sulfonated polystyrene.

Samples were compression molded at 700 bar into 32 mm disks at elevated temperature. The amount of sample was adjusted to obtain the proper thickness for EXAFS measurements; thicknesses in most cases were between 1 and 2 mm. Samples used for change in weight measurements were much thinner to speed mass transfer; typical thicknesses were 0.2 mm. Samples were completely dried before water absorption. Completely dried means that no more water could be removed at the specified drying conditions which were 70 °C and a vacuum oven for E−MAA ionomers and 150 °C in atmosphere for SPS ionomers. In both cases, it is believed that all water was removed from the samples because a slight increase in drying temperature did not change the equilibrium dry weight significantly. However, it is impossible to know with absolute certainty that all water was removed, since the polar groups have a very strong energetic interaction with water, and to remove all water with heat and vacuum may not be possible. No water was absorbed by the unneutralized acid copolymers within the error of the change in weight measurement, indicating that essentially all water absorbed was associated with the metal cation.

Samples were immersed in deionized water for a specified length of time, and excess water was removed via a paper towel

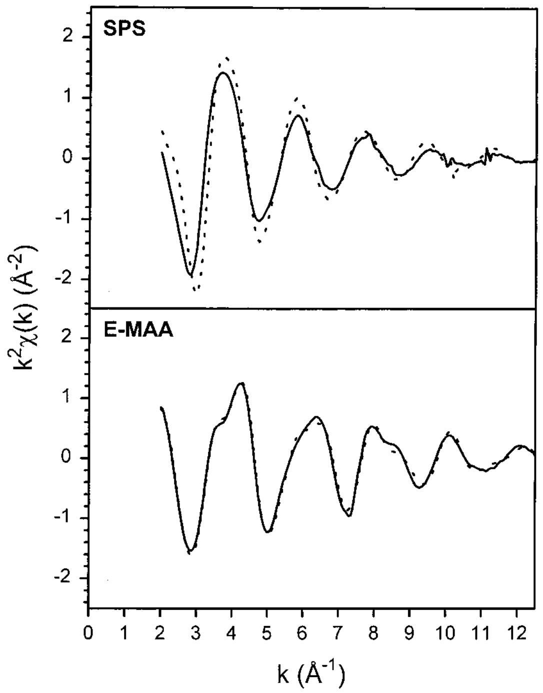


Figure 3. Plots of $k^2\chi(k)$ vs k for wet (dashed line) and dry (solid line) ionomers. The water/zinc ratios are approximately 0.4:1 for the E−MAA ionomer and 5.3:1 for the SPS ionomer. The E−MAA ionomer was made from a copolymer having 3.9 mol % acid repeat units with 57% of the methacrylic acid residues neutralized with zinc. The SPS ionomer had 3.4 mol % substitution of acid groups in the benzene ring, and the acid groups were stoichiometrically neutralized with zinc.

before further sample handling. Except for Karl Fischer analysis on the samples provided by DuPont, the number of water molecules absorbed per zinc atom was calculated by measuring the change in weight of the sample and assuming that the fully dried sample did not contain any water. For EXAFS samples, immediately after being weighed the samples were transferred into sealed bags and shipped in a liquid nitrogen dewar to the Stanford Synchrotron Research Laboratory (SSRL). Samples in sealed bags provided by DuPont were also shipped in the liquid nitrogen dewar. At SSRL the bags were cut and then immediately placed inside a glovebox to warm to room temperature. Immediately after warming to room temperature, samples were then loaded into the sample holder and cooled to liquid nitrogen for measurement. Fully hydrated samples were shipped at room temperature in water. It is certainly possible that the water content shifted inside the glovebox, so nonzero or non-fully-hydrated water contents quoted for EXAFS measurements should be regarded as only approximate.

The procedures for data collection and reduction are given in the preceding paper.[5]

Results and Discussion

Representative $k^2\chi(k)$ vs k spectra for wet and dry E−MAA and SPS ionomers are shown in Figure 3. Wet samples have been soaked in deionized water at room temperature until the weight of water + polymer is constant with soaking time. The time required to reach equilibrium for all samples was no more than a couple of days. Figure 3 shows the high data quality achieved in this experiment. To better visualize how changes in structure affect the arrangement of atoms around zinc, radial structure functions (RSFs) were calculated and will be presented throughout the remainder of this paper. Figure 4 shows RSFs for the k-space spectra presented in Figure 3. Error bars represent one standard deviation calculated by averaging standard deviations for three different E−MAA samples measured at least three times each.[16] The errors in these experiments have the same functional dependence and slightly lower magnitude compared to the error for PtO_2 spectra measured by Vaarkamp.[17] The effect of water on these two materials indicates clear qualitative differences between the two anions, and these differences will be explored below.

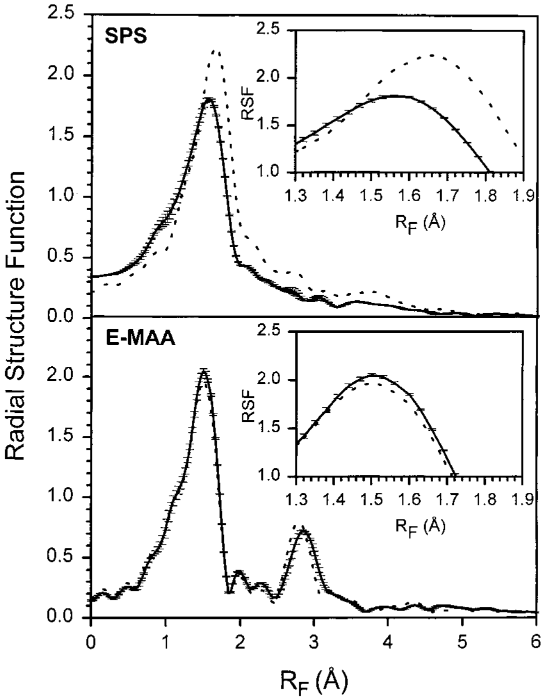


Figure 4. Radial structure functions for wet (dashed line) and dry (solid line) ionomers of Figure 3.

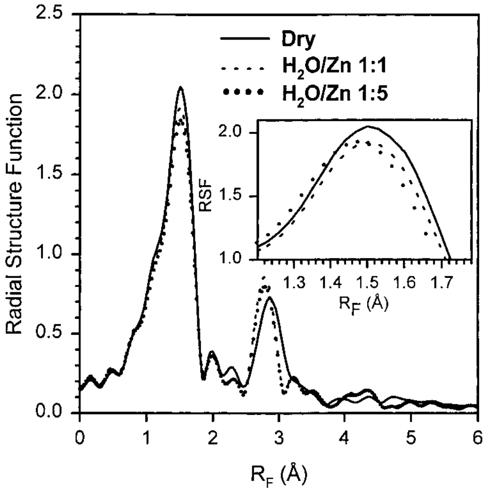


Figure 5. Radial structure functions at the indicated water/zinc ratios for E−MAA ionomer. This ionomer was made from a copolymer having 3.9 mol % acid repeat units with 57% of the methacrylic acid residues neutralized with zinc. These samples were prepared in a humidity chamber, and the amount of water was determined by Karl Fischer analysis.

The consistency in position of the first-shell peak for the carboxylate material clearly shows that the average zinc−oxygen distance remains at approximately 1.96 Å; hence, the hydrated material also has four oxygen atoms coordinated to zinc. Figure 5 indicates that the amount of water does not have a large effect on the EXAFS

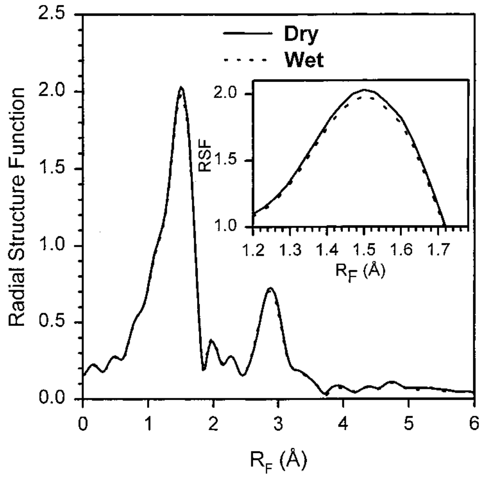


Figure 6. Radial structure functions for wet and dry E−MAA ionomer made from a copolymer having 4.2 mol % acid repeat units with 38% of the methacrylic acid residues neutralized with zinc. The water:zinc ratio was approximately 0.5:1. The change in the second-shell peak with absorbed water is different than the change in Figure 4 or 5.

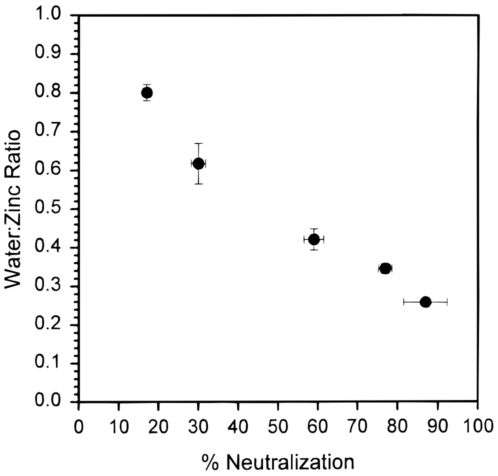
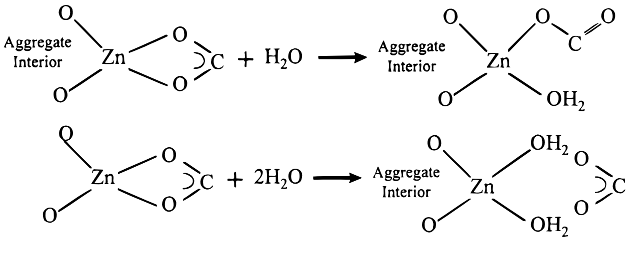


Figure 7. Amount of water absorbed as a function of percent neutralization for E−MAA ionomer made from a copolymer containing 3.9 mol % acid groups. The lowest neutralization level (17%) represents a copolymer with 3.6 mol % acid groups. The *x* error bars were determined from duplicate EMPA measurements while *y* error bars were determined by duplicate water absorption measurements.

pattern for a zinc ionomer with 57% neutralization; however, there are some changes in the second peak at $R_F \approx 3$ Å and subsequent higher-order features. Figure 6 shows the result for a different base copolymer with 4.2 mol % acid repeat unit and 38% zinc neutralization; the shift in the second-shell peak is almost nonexistent. A sample with 7.5 mol % acid repeat unit and 34% zinc neutralization also showed very little change in the second shell with the addition of water. For all three materials, however, the first-shell peak decreased in magnitude slightly, indicating an increase in mean-squared variation of the zinc−oxygen distances.

The rather small changes in EXAFS patterns for all of these samples indicate that water does not replace carboxylate oxygens in most zinc atoms. In other words, no large-scale atomic rearrangements occur in the vicinity of zinc, and the aggregates do not break up. The drop in first-shell peak height does represent a small increase in the mean-squared displacement of oxygen atoms around zinc. We believe these changes are due to bidentate water replacing chelating carboxylate anions at the edges of an aggregate according to one of two currently indistinguishable possibilities:



This transformation occurs only with zinc atoms at the edge of an aggregate; interior zinc atoms coordinated with oxygens from four different carboxylate anions are unaffected. Since zinc−oxygen distances are altered at the edge of an aggregate due to water replacing carboxylate oxygens, the overall variation of the zinc−oxygen distance around its average value increases slightly. More difficult to explain are the qualitative differences in second-shell behavior represented by Figures 5 and 6. Even though the average patterns for the dry samples are almost identical, it is possible that the distributions of aggregate sizes are different, causing qualitatively different behaviors. Also difficult to explain is the relative insensitivity of the EXAFS pattern at $R_F > 3$ Å with water content shown in Figure 5; however, it is not possible to really know exactly how the EXAFS pattern would be affected with amount of water absorbed if water absorption is only at the edges of an aggregate.

If water adds only to aggregate edges, then the amount of absorbed water should decrease with increasing neutralization level since the size of the aggregates increases with neutralization level.[4] Figure 7 shows exactly this trend and has other salient features. Assuming interior zinc atoms have the arrangement of atoms presented in Figure 2 and with the constraint that all zinc atoms be either 4- or 2-fold coordinated to carboxylate oxygens,[18] a series of allowed structures are shown in Figure 8 in order of increasing zinc aggregation number. The water:zinc ratio if all edge zinc atoms are coordinated to one water molecule is also shown. An extrapolated water:zinc ratio of 0.2 at 100% neutralization from Figure 7 corresponds to a zinc aggregation number of approximately 100. If all zinc atoms in a single aggregate lie in a plane, the aggregate radius would be approximately 3.5 nm. On the basis of the magnitude of this value, it seems more likely that one water molecule rather than two replace a carboxylate anion at the edge of an aggregate. Of course, this calculation assumes that the drying procedure used in this study completely removed water.

The size of aggregates in zinc-neutralized E−MAA ionomers was directly measured using scanning transmission electron microscopy (STEM) as described in a recent paper.[19] Two samples of a material with 5.5 mol % acid groups were measured: one with 58% zinc neutralization and one with 22% zinc neutralization. In contrast to the current study, these authors found no change in the aggregate size with neutralization level. The micrographs appear to show an increase in the number density of aggregates with neutralization level; however, the samples were not controlled for thickness so this increase could have been due to a thicker section being imaged. The size of aggregates was found to be

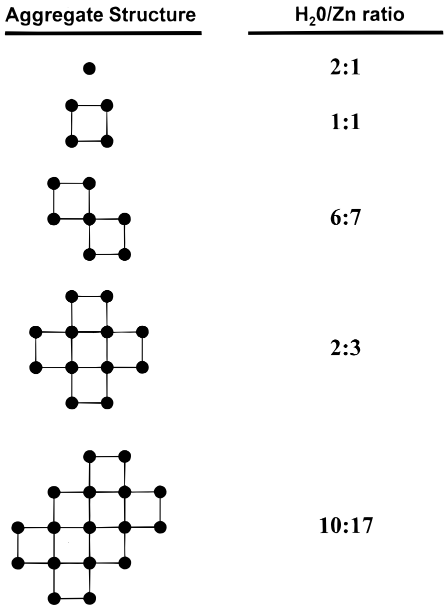


Figure 8. Schematics of aggregate structures with the constraint found in the discussion; each filled circle represents a zinc atom. On the right is the water/zinc ratio if all edge zinc atoms are coordinated to one water atom. The schematic with a H_2O/Zn ratio of 6:7 corresponds to the structure shown in Figure 2.

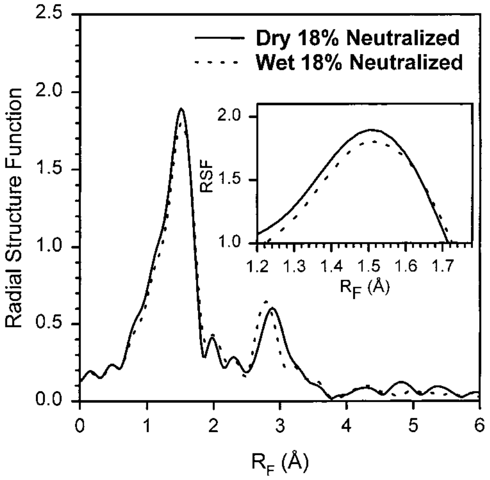


Figure 9. Radial structure functions of dry and wet E−MAA ionomer made from a copolymer having 3.6 mol % acid repeat units and with 17% of the acid repeat units neutralized with zinc.

2.5 ± 0.5 nm, which is the same size range given in this paper.

The water:zinc ratio should extrapolate to at least 2 at 0% neutralization since all zinc atoms would be isolated. Even in the dry state, an unaggregated zinc atom would not necessarily have the same oxygen coordination environment as an aggregated zinc atom, and hence changes in the EXAFS pattern might be noticeable. In another publication,[4] an ionomer with only 17% of the acid groups neutralized was shown to have both isolated zinc ions and aggregated zinc ions, while for neutralization levels greater than 30% all zinc ions were in aggregates. When water is added to the 17% neutralization level ionomer, the change is actually very similar to that found for other ionomers as shown in Figure 9. The spectra shown for the wet polymer correspond to a material with only half of the maximum amount of absorbed water. For isolated zinc atoms as well as for aggregated zinc atoms, water is most likely replacing chelated carboxylate oxygen atoms. Also, in Figure 7 an upturn in slope should occur between 30% and 17% neutralization so the graph begins to extrapolate toward at least 2. The error in the measurement does not preclude such a possibility; however, this upturn is not clearly noticeable either.

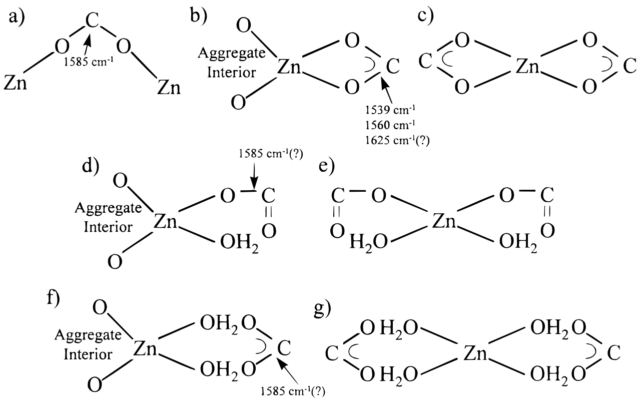


Figure 10. Possibilities of carboxylate−zinc environments that could theoretically have different infrared absorption frequencies. Letters correspond to letters in the text. Only seven of the nine listed in the text are shown here; possibilities 8 and 9 (h and i) are the hydrogen-bonded counterparts of (d) and (e), respectively. The frequency values represent the band assignments made in this paper.

The interpretations presented in this paper should be consistent with infrared data presented in the Introduction. Infrared data and the resulting interpretation are not unambiguous, because of the large number of overlapping bands and the inherent problems in trying to resolve multiple peaks. Even without frequency splitting and ignoring bands that occur in the un-ionized copolymer, potentially nine different frequencies for a single carboxylate vibrational mode could occur in zinc ionomers as shown in Figure 10: (a) a carboxylic acid coordinated to two zinc atoms in the interior of an aggregate, (b) a carboxylic acid chelated to zinc at the exterior of an aggregate, (c) a carboxylic acid chelated to an isolated zinc atom, (d) a carboxylic acid with one oxygen atom coordinated to zinc at the edges of an aggregate, (e) a carboxylic acid coordinated with one oxygen atom to an isolated zinc atom, (f) a carboxylic acid near two water molecules coordinated to zinc at the edge of an aggregate, (g) a carboxylic acid near two water molecules coordinated to an isolated zinc atom, and (h, i) possibilities (d) and (e) hydrogen bonded to a free carboxylic acid. Since only two or three bands are present, some of these bands are almost certainly not important and/or infrared-active. For example, most free carboxylic acid groups are dimerized in the dry E−MAA ionomer;[12] hence, possibilities (h) and (i) are probably not present in significant concentration. Also, the infrared frequencies would probably not be different for an isolated zinc atom and a zinc atom at the edge of an aggregate (i.e., possibilities (b) and (c), possibilities (d) and (e), as well as possibilities (f) and (g)). Previous infrared studies have not reported any band shifting at low neutralization; however, it is possible that isolated ions were not present in sufficient concentration.

The following assignments are based on the results from EXAFS work and the behavior of infrared bands described in other papers. These assignments are not based on any normal-mode calculations; rather these assignments are based on the coordination environments found in this EXAFS study and are consistent with each other and results from other studies.

The band at 1585 cm^{-1} is assigned to interior bidentate tetrahedrally coordinated zinc atoms. In the assignment given by Painter and Coleman,[12] this band was assigned to bidentate, *chelated* tetrahedrally coordinated zinc atoms. EXAFS spectra clearly and unambiguously indicate no hexacoordinated zinc atoms; instead, the bands that occur at 1539 and 1560 cm^{-1} and perhaps the band at 1625 cm^{-1} are assigned to carboxylate anions chelated to zinc at the edges of the aggregates. This study cannot comment on the formation of acid salts although high-temperature experiments are currently in progress.

The bands at 1539 and 1560 cm^{-1} (and perhaps the band at 1625 cm^{-1}) become weaker relative to the 1585 cm^{-1} band as the neutralization level becomes higher[12] since the aggregates become larger and hence edge carboxylate anions become a much smaller fraction of the total. Also, in the fully neutralized material the doublet becomes weaker upon heating, and the 1585 cm^{-1} band becomes stronger and shifts toward lower wavenumber.[12] Consistent with the interpretation presented in the current paper is that the zinc aggregates become bigger during heating. Doublet intensity cannot be recovered by cooling to room temperature as would be expected.

The change in spectra as a partially neutralized sample is heated above 100 °C for many days[12] is more difficult to explain. In this experiment, the doublet (or triplet) increases in intensity, and the band at 1585 cm^{-1} decreases in intensity. Without some fundamental change in aggregate structure which only occurs in partially neutralized materials (not addressed by this current study), the only explanation is a reduction in the average size of the aggregates. Although this hypothesis seems counterintuitive on the basis of the results for the fully neutralized material, it is certainly possible depending on the relative importance of crystallization and ionic aggregation for this particular sample. Also, if water were present in the unheated sample, this behavior would be expected on the basis of the reasoning presented in the next paragraph. The possibility of water absorption by the samples in these experiments cannot be discounted on the basis of the disagreement between this study and the Ishioka[13] study.

As water is added to a partially neutralized material, the doublet (or triplet) becomes weaker as chelated carboxylate anions disappear. The band at 1585 cm^{-1} gains in intensity with added water, and hence this band also represents either structure d or f in Figure 10. In other words, this vibrational frequency just happens at or near the vibrational frequency of an interior bidentate carboxylate anion. For a fully neutralized material, the amount of edge carboxylate anions is a small amount of the total, and hence any changes are small.[13]

The behavior of SPS ionomers with added water is entirely different. SPS ionomers absorb much more water than E$-$MAA ionomers. Fully hydrated ionomers with 3.4 and 5.7 mol % acid groups fully neutralized with zinc both have water:zinc ratios of 5.3:1 according to change in weight measurements. Ionomer EXAFS patterns as a function of water content are shown in Figure 11. The first peak shifts toward higher R_F as the water content increases, clearly indicating that the zinc coordination number increases. Zinc benzenesulfonate hexahydrate has six water molecules surrounding zinc,[20] and spectra from the fully hydrated samples were fit using atomic positions from the crystal structure of zinc benzensulfonate hexahydrate. The first-shell oxygen atoms in the latter are widely separated (Zn$-$O distance range from 1.98 to 2.23 Å), and two overlapping peaks appear in the simulated spectra while only one peak is found in the spectrum for the fully hydrated material. Since the structure of the fully hydrated material was not described by the crystal structure of zinc benzenesulfonate, further simulations were performed with FEFF. These simulations indicated that the average zinc$-$oxygen distance is 2.09 Å, but not all six oxygen atoms are at this distance since the mean-squared displacement is too large. The mean-squared variation in distance is consistent with a Zn$-$O distance range of approximately 0.07 Å. Hence, water probably fully hydrates zinc atoms in the sulfonate ionomer with significant variation in the Zn$-$O distances. However, it is certainly possible that some zinc ions are coordinated to four water molecules and two oxygens from sulfonate groups.

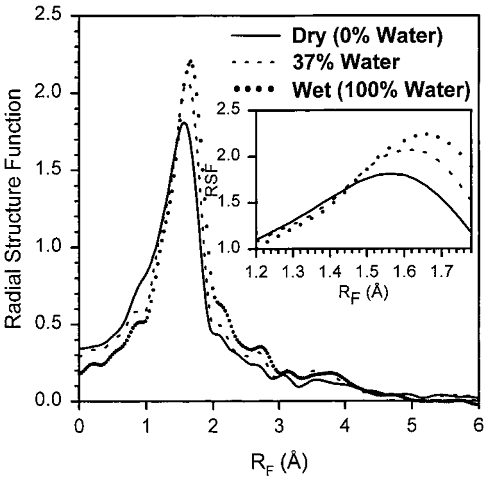


Figure 11. RSF for SPS as a function of water content. Benzene (3.4 mol %) rings had covalently bonded sulfonate groups, and the acid groups were stoichiometrically neutralized with zinc.

Summary

Water absorption causes qualitatively different changes in the EXAFS spectra of zinc-neutralized sulfonate and carboxylate ionomers consistent with the amount of water each material will absorb. In sulfonate ionomers, zinc will absorb almost six water molecules per zinc atom, and the EXAFS pattern is consistent with zinc coordinated to six oxygen atoms. In carboxylate ionomers, approximately an order of magnitude less water is absorbed per zinc atom. EXAFS patterns indicate only very small changes in zinc local environment occur with water absorption, which is consistent with water only being present at the edges of an aggregate. As the zinc content decreases, the amount of water absorbed per zinc ion increases since the average aggregate size becomes larger. At very low neutralization levels, isolated zinc ions cause significant changes in the dry ionomer EXAFS pattern; however, the effect of adding water is similar to the effect adding water has in a material that contains only aggregated zinc ions. The results presented in this paper for the carboxylate materials are interpreted in light of infrared data appearing in the literature, and new band assignments are given that are consistent with both EXAFS data and infrared data.

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