EXAFS Studies of Various Sulfonated and Carboxylated Cadmium Ionomers

Brian P. Grady*,† and Robert B. Moore‡

School of Chemical Engineering and Material Science, University of Oklahoma, 100 East Boyd, Norman, Oklahoma 73019-0628, and Department of Polymer Science, The University of Southern Mississippi, Southern Station, Box 10076, Hattiesburg, Mississippi 39404-0076

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ABSTRACT: Four sulfonate ionomers and one carboxylate ionomer, all neutralized with cadmium, were studied using the technique of extended X-ray absorption fine structure (EXAFS) spectroscopy. The cadmium in all four sulfonate ionomers had essentially identical EXAFS oscillations, which suggests that the influence of the identity of the polymer matrix on the local aggregate structure is minimal. In contrast, the cadmium in the carboxylate ionomer had a substantially different local environment, showing that, as expected, the local environment of the cadmium cation depends on anion type. For the sulfonate ionomers, simulations of the EXAFS oscillations with reasonable fitting parameters using the crystal structure of cadmium methanesulfonate dihydrate fit the experimental patterns very well. This agreement between theory and experiment strongly suggests that the atomic arrangement around the cadmium atom in the ionomer is the same as the arrangement around the cadmium atom in the small-molecule analogue. In the carboxylate ionomer, small but significant differences existed between the experimental pattern and the pattern generated theoretically using atomic positions derived from the small-molecule analogue cadmium acetate dihydrate. The reason for the difference is unclear; however, if the atomic positions in the ionomer were only slightly different from those in the crystal structure, this could have led to the disagreement between the experimental data and the fit.

Introduction

The remarkable improvement in mechanical properties of polymers having a small number of ionic groups covalently bonded to the polymer backbone is due to phase separation of the ionic groups into nanometer-size ionic-rich aggregates. The aggregates act as both reinforcing filler and cross-links, leading to improvement in such properties as mechanical strength, abrasion and tear resistance, and impact strength.[1] The fundamental driving force for phase separation in these systems is the favorable energetics of ionic group association. The work described in this paper is designed to elucidate the internal atomic structure of these aggregates.

Extended X-ray absorption fine structure (EXAFS) is the measure of oscillations in the X-ray absorption coefficient on the high-energy side of an absorption edge. The absorption coefficient generally decreases slowly as X-ray energy is increased, except at an absorption edge where the energy of the X-ray is just sufficient to cause the ejection of a core electron from a constituent atom. The atom absorbs the X-ray and a large increase in the absorption coefficient results. On the high-energy side of the absorption edge, the ejected electron can be backscattered by atoms around the absorbing atom. Oscillations in the absorption coefficient are caused by interference between the outgoing and backscattered electrons. The shape and period of the oscillations are a function of the absorbing atom as well as the type, distance, and number of atoms around the absorbing atom.

At sufficient energies (greater than 60 eV) above the edge, the process can be described by single-electron single scattering theory, which was originally developed by Stern et al.[2] The fundamental equation from this theory assuming a completely isotropic sample or assuming completely depolarized radiation is

$$\chi(k) = \frac{\mu(E) - \mu_0(E)}{\mu_0(E)} = \sum_j N_j {S_0}^2 \frac{F_j(k)}{k{R_j}^2} \mathrm{e}^{-2\sigma_j^2 k^2} \mathrm{e}^{-2R_j/\lambda_j} \sin[2kR_j + \phi_{ij}(k)] \quad (1)$$

where $\mu(E)$ and $\mu_0(E)$ are the measured and mean absorption coefficients at the energy E, N_j is the number of atoms of type j in the jth shell, S_0^2 is the amplitude reduction factor which is due to excitations of electrons other than 1s electrons (for a K-edge) in the X-ray absorbing atom, $F_j(k)$ is the backscattering amplitude (called the amplitude function) from the type j atoms, R_j is the root mean square distance between the central atom and the atoms in the jth shell, σ_j is the Debye−Waller factor, which measures the variation in R_j about its mean and includes thermal vibrations as well as average variations in distance of each atom in the jth shell, λ_j is the electron mean free path, and ϕ_{ij} is the phase shift (called the phase function) experienced by the photoelectron, which is a function of both the absorbing i atom and backscattering atoms of type j. k is termed the wavevector because $2\pi/k$ is the wavelength of the ejected photoelectron.

This paper describes EXAFS experiments which were used to determine the cation local environment in cadmium ionomers. A previous study[3] of cadmium-neutralized sulfonated polystyrene containing 6.05 mol % sulfonate groups concluded that the cadmium cation was sixfold coordinated to oxygen at a distance of 2.34 Å. Detailed modeling suggested that four of the oxygens were from sulfonate anions and two were from water. This study also highlighted the risk of analyzing each feature individually. Because the EXAFS effect results in sinusoidal oscillations of the absorption coefficient,

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* Author to whom correspondence should be addressed.

† University of Oklahoma.

‡ The University of Southern Mississippi.

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backscattered waves from two different shells can interfere with each other and change the amplitude that would be expected from an isolated shell according to eq 1. It was shown that the backscattering amplitude of the sulfur atoms in the second shell was reduced due to destructive interference between second-shell sulfur atoms and atoms in higher coordination shells.

In this study, five different ionomers were tested, four having a benzene sulfonate anion and the other having a carboxylate anion. The cadmium local environments in the sulfonate ionomers were found to be essentially identical to each other. The local environment around the cadmium in the carboxylate ionomer differed from the local environment in the sulfonate ionomers.

Experimental Section

The four different sulfonate ionomers tested were two sulfonated polystyrenes (SPS), one containing 5.7 and the other 3.4 mol % sulfonate groups, a commercial polyester ionomer from Eastman Chemical termed AQ-55 (polymerized from a copolymer of isophthalic acid, sulfoisophthalic acid, diethylene glycol, and cyclohexanedimethanol) having a sulfur content of 2.1 wt %, and an experimental polyester ionomer (X-21916) from Eastman Chemical having the same components with 7 mol % sulfonate groups. The carboxylate ionomer was an ethylene−methacrylic acid (E−MAA) copolymer containing 3 mol % acid groups. Preparation of the cadmium form for each ionomer is discussed below.

The acid forms of the SPS ionomers were synthesized according to the procedure described by Lundberg et al.[4] The approximate sulfonation efficiency was 75% based on titration using methylene blue as an indicator. The acid ionomers were Soxhlet extracted using water for 72 h after the synthesis, before drying at room temperature for 1 week in a vacuum oven. A 10 wt % solution of the polymers was prepared by dissolving roughly 10 g of polymer in a 90/10 v/v mixture of toluene/methanol and neutralized with a stoichiometric amount of cadmium hydroxide hydrate dissolved in methanol. The resulting cadmium-neutralized materials were dried in air and then dried for 1 week in a vacuum oven at room temperature.

The polyester ionomers were supplied in the sodium sulfonate form and ion-exchanged to the cadmium sulfonate form using the following procedure. Ten gram samples of the ionomers were dissolved in 2000 mL of deionized water at 90 °C. An aqueous solution of cadmium acetate dihydrate (at a 2.5 times molar excess relative to the sulfonate groups) was slowly added to the dilute polymer solution with vigorous stirring. The mixture was stirred for 1 h, during which time the divalent cadmium ions exchanged with the monovalent sodium ions. This ion-exchange procedure resulted in the formation of physical cross-links which caused the polymers to precipitate from solution. The fine precipitates were filtered, rinsed with deionized water, and then stirred in fresh hot deionized water for 2 h. This filtering/washing procedure was repeated twice in order to completely remove excess cadmium atoms. The washed cadmium ionomers were then dried at 40 °C in a vacuum oven for 5 days.

The acid form of E−MAA was neutralized following a procedure described previously,[5] but with some modification. Approximately 15 g of the polymer was dissolved in 2000 mL of a 4/1 v/v mixture of mixed xylenes/dimethyl sulfoxide at 120 °C. The mixture was vigorously mixed in a stirred reflux apparatus using a nitrogen sparge to prevent oxidation. Unlike the procedure described previously, all of the polymer seemed to dissolve under these conditions. A stoichiometric amount of salt was added, and the polymer/salt solution was mixed for 2 h under these conditions. Most of the lower boiling xylene was then distilled, with the polymer precipitating during the distillation. The polymer was separated from the remaining solvent, dried under a hood for 1 week, and then dried in a vacuum oven at 90 °C for another week. Although no characteristic DMSO smell was noticed after this drying procedure, electron microprobe analysis (EMPA) indicated that a very small amount of DMSO was still present (~0.3 wt %). EMPA also confirmed that the neutralization was stoichiometric.

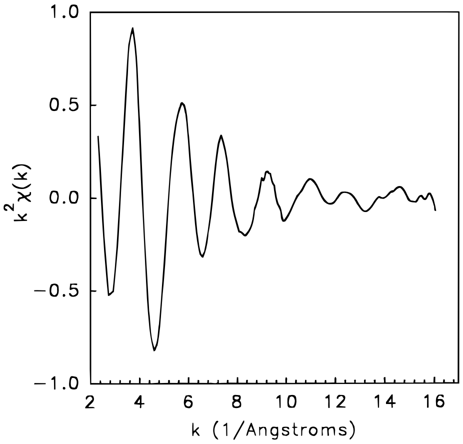

Figure 1. $k^2\chi(k)$ vs k plot for 3.4 CdSPS.

Samples were compression molded at 10 000 psi into 32 mm disks using a mold purchased from Buehler Inc. Molding temperature for the polyester ionomers was 120 °C, for the E−MAA ionomers 140 °C, and for the sulfonated polystyrene ionomers 165 °C. A small amount of mold release agent (Miller-Stephenson Co.) was used to facilitate removal of the pressed disks from the mold. The thickness of all samples was approximately 5 mm. Finished samples were then dried in a vacuum oven for another week at room temperature and then stored in a vacuum desiccator until immediately before measurement.

Measurements were made at the Stanford Synchrotron Radiation Laboratory on Beamline 7−2. Steps of 5 eV were used in the preedge region and the EXAFS region, while 2 eV steps were employed from 11 eV below the edge to 80 eV above the edge. Entrance slits of 0.3 mm were used to obtain high-energy resolution. Energy calibration was performed with the 5.7 CdSPS sample. Ionization chambers (15 cm) filled with argon were used to monitor the incoming and outgoing intensities of X-rays. A total of six scans (each scan lasted approximately 20 min) were collected, and these scans were added after E_0 determination before further data analysis to improve the signal-to-noise ratio.

AUTOBK,[6] a commercial software package available from the University of Washington UWXAFS project, was used to convert the measured μt vs E curves to $k^2\chi(k)$ vs k. To help this program determine the optimal background subtraction and edge locations, a hypothetical Cd−O structure with six oxygens at 2.30 Å was modeled using the simulation package FEFF6,[7] also available from the University of Washington. This package performs *ab initio* calculations of EXAFS patterns based on user-supplied *XYZ* coordinates of the atomic structure and includes single- and multiple-scattering curved wave paths. After isolation of the EXAFS oscillations, the data were Fourier transformed, which gave a result termed the radial structure function (RSF). The radial structure function is similar to a radial distribution function because peaks in the RSF usually correspond to distinct coordination shells. The abscissa of the RSF has units of angstroms, but the location of the peaks are shifted from the real distances as indicated in eq 1; hence a subscript F will be used to distinguish this distance from the actual interatomic distance R. Reduction procedures for all data sets were identical to enable direct comparison of results.

One of the most significant user-supplied parameters for the new data reduction procedure is the k-space truncation points. In particular, determining the high-k truncation point was difficult as shown in Figure 1. Many of the references in this text to changes in background subtraction procedure refer simply to changing the upper truncation point. Although the oscillations become less sinusoidal above $k \approx 12$ Å^{-1}, it was felt that $k = 16$ Å^{-1} was an appropriate truncation point because more of the data was used. Truncating at $k = 12$ Å^{-1}

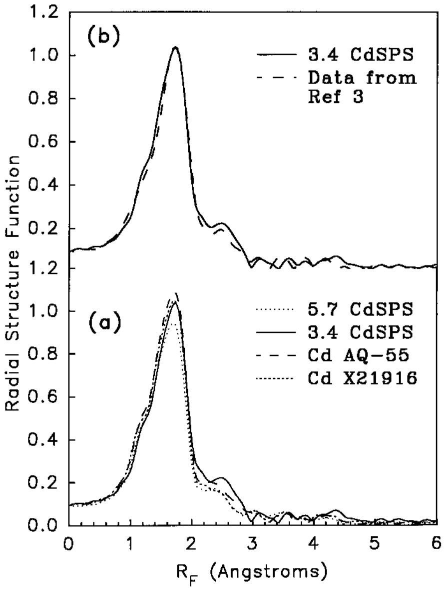

Figure 2. Radial structure functions for sulfonate ionomers: (a) sulfonate ionomers examined in this study; (b) a comparison of 3.4 CdSPS collected in this study and a 6.05 CdSPS from ref 3. The RSF in part b is different from those in ref 3 because of the background procedure and the manner in which the software performs the Fourier transform.

eliminates the shoulder in the RSFs near $R_F = 1.2$ Å and most of the fine detail for features above $R_F = 3$ Å.

Fitting of the data to model structures was performed using FEFFIT from UWXAFS in combination with FEFF6. Model structures will be discussed in detail in the next section; however, the basic procedure was to thoroughly search the literature for a similar small-molecule compound and use this structure to create an input file for FEFF6. The software FEFFIT was used to determine the best fit results by allowing the Debye–Waller factors and edge energy to vary.

Results and Discussion

Radial structure functions for the sulfonate ionomers are shown in Figure 2. For all the ionomers except 5.7 CdSPS, the first-shell peaks (centered near $R_F = 1.6$ Å) are essentially identical, which indicates that the type, distance, and number of atoms in the first shell are also identical. Also in Figure 2, a comparison is shown between the 3.4 CdSPS in this study and the results of a 6.05 CdSPS sample presented in a previous study.[3] The features near $R_F = 2.4$ Å are similar for all the sulfonate ionomers, although small differences do exist. Based on the general agreement between all of these EXAFS patterns, it is likely that the local environments are identical for all the sulfonate ionomers.

Before discussing the structures in Figure 2 more closely, it is instructive to examine Figure 3, which compares the EXAFS results for the sulfonate and carboxylate ionomers. The large differences in the radial structure functions indicate that the local structure around the cadmium atom is significantly different in the carboxylate ionomer. Not only is there a clear difference in the first shell, but even more convincing are the qualitative changes at higher R_F. The changes at higher R_F are not due to the method of background subtraction. Different background methods identically applied to the experimental data always gave the same qualitative result, namely that the RSFs of the sulfonate ionomers are very similar to each other while the RSF for the carboxylate ionomer is very different.

The difference in height of the first-shell peak for the 5.7 CdSPS relative to the other sulfonate ionomers could indicate a change in the local environment. However, it is not clear that the differences shown in Figure 2 are outside of normal experimental error. If the data reduction procedure described in previous papers[3,8] is used, the EXAFS pattern of the 5.7 CdSPS is not outside the experimental error determined previously.[8] Further, differences in peak height are reflected in the quality of the fit and the E_0 value, not in the Debye–Waller factor, which suggests that the local environment in the 5.7 CdSPS is not significantly different from that of the other sulfonate ionomers.

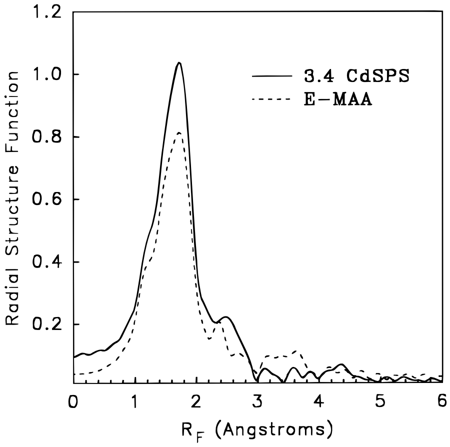

Figure 3. Radial structure functions for the sulfonate ionomer 3.4 CdSPS and the carboxylate ionomer Cd E–MAA. Compare Figures 3 and 2.

The results of this work suggest that the local structure first presented in a previous paper was essentially correct.[3] Cadmium methanesulfonate dihydrate, $Cd(CH_3SO_3)_2{\cdot}2H_2O$,[9] has a chemical formula analogous to the local chemical formula for the cadmium ionomer; the only substantial change is that the aromatic group plus polymer chain is replaced by CH_3 groups. The crystal structure for the aromatic cadmium sulfonate or the longer chain hydrocarbon cadmium sulfonate could not be found in the literature. Table 1 lists the atomic positions for the atoms around the central Cd atom in cadmium methanesulfonate dihydrate; the unit cell is triclinic with space group $P\bar{1}$. None of the atomic positions listed in Table 1 would necessarily change with the bulky aromatic group instead of a CH_3 group because no space overlap of atoms exists due to the limited distances represented in Table 1. Further evidence supporting the hypothesis that cadmium is surrounded by two water molecules is that the equilibrium water content of the cadmium methanesulfonate at room temperature and pressure is the dihydrate; heating to 90 °C releases one water of hydration and to 130 °C releases the other.

FEFF simulations and best fits of the structure using the atomic positions of cadmium methanesulfonate dihydrate are shown in Figure 4 for 3.4 CdSPS. In this curve-fitting procedure, the first-shell oxygen and second-shell sulfur Debye–Waller factors were adjustable, while the remainder of the higher shell Debye–Waller factors were arbitrarily set to 0.007 Å^2. Changing these higher shell Debye–Waller factors essentially had no impact on the quality of fit. The amplitude reduction parameter could be set to 1.0 in this simulation, which was not the case if the background procedure discussed in ref 3 was used. Allowing $S_0{}^2$ to vary improved the agreement between theory and experiment slightly; however, in all cases, the range of the error in the determination of the amplitude reduction factor in-

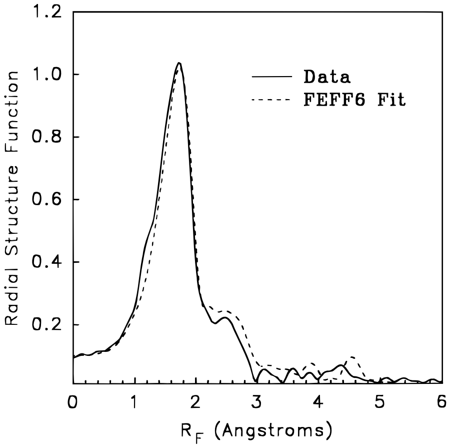

Figure 4. FEFF simulation for 3.4 CdSPS using the atomic positions derived from cadmium methanesulfonate dihydrate. Debye–Waller factors are shown in Table 2.

Table 1. Atomic Coordinates for Cadmium Methanesulfonate[9]

X (Å)	*Y* (Å)	*Z* (Å)	Cd–atom dist (Å)	atom type
0	0	0	0	Cd
1.4688	−0.5137	1.6394	2.2603	O
−1.4688	0.5137	−1.6394	2.2603	O
0.5572	−1.7227	−1.3689	2.2698	O
−0.5572	1.7227	1.3689	2.2698	O
−1.5541	−1.401	0.9422	2.2947	O
1.5541	1.401	−0.9422	2.2947	O
2.3694	−1.6655	1.7031	3.3598	S
−2.3694	1.6655	−1.7031	3.3598	S
−2.3732	−1.3031	2.1467	3.4552	S
2.3732	1.3031	−2.1467	3.4552	S
−3.1884	1.7633	−0.4986	3.6775	O
3.1884	−1.7633	0.4986	3.6775	O
1.3018	0.9837	−3.498	3.8599	C
−1.3018	−0.9837	3.498	3.8599	C
−3.2738	−0.1514	2.0831	3.8833	O
3.2738	0.1514	−2.0831	3.8833	O
1.6812	−2.8961	1.9728	3.8866	O
−1.6812	2.8961	−1.9728	3.8866	O
−1.6812	−3.2019	−1.9728	4.1195	O
1.6812	3.2019	1.9728	4.1195	O
4.1853	1.3604	0.9253	4.497	O
−4.1853	−1.3604	−0.9253	4.497	O
−0.5572	−4.3753	1.3689	4.6182	O
0.5572	4.3753	−1.3689	4.6182	O
−3.0613	−2.5338	2.4164	4.6509	O
3.0613	2.5338	−2.4164	4.6509	O
4.7425	−0.3623	−0.4437	4.777	Cd
−4.7425	0.3623	0.4437	4.777	Cd

cluded 1.0. Therefore, only three adjustable parameters were used in the fits of experimental data to theory for the sulfonate ionomers: two Debye–Waller factors and the edge energy (in the FEFFIT documentation, it is strongly suggested that E_0 be allowed to float to correct for problems such as incomplete core–hole shielding, angular variations in valence charge distribution, and charge transfer effects). However, as commented in ref 3, the location of the first-shell peak as determined by FEFF suggests a Cd–O distance of 2.30 Å. Since the average value of the first-shell Cd–O distance according to Table 1 is roughly 2.28 Å, all of the atomic positions in the fit were shifted by 0.02 Å so that the maxima of the first-shell peaks were identical for the simulation and the experimental data.

Best fit results for the first- and second-shell Debye–Waller factors using the cadmium methanesulfonate dihydrate crystal structure to fit the sulfonate ionomer experimental EXAFS data are shown in Table 2. The error between experiment and theory was minimized in R_F space for the range R_F = 1.25–3.25 Å. The corresponding RSFs are shown in Figure 4 for 3.4 CdSPS. In all cases, the agreement between the data and the theory was better than 2.3 parts in 1000; in the case shown in Figure 4, the agreement is 1.75 parts per 1000. The E–MAA data were also fit to the same sulfonate model to show that statistically this RSF was different from the RSFs for the sulfonate ionomers. Using the results of the sulfonate ionomers to calculate a mean and standard deviation, the Debye–Waller factors for the E–MAA were outside the 99% *t*-statistic confidence interval. Furthermore, the quality of the fit, particularly between R_F = 2 Å and R_F 3.25 Å, was extremely poor.

Table 2. Debye–Waller Factors for Simulations with Cadmium Methanesulfonate Dihydrate

ionomer	shell 1 (Å^2)	shell 2 (Å^2)
6.05 CdSPS	0.0095	0.0154
5.7 CdSPS	0.0096	0.0138
3.4 CdSPS	0.0093	0.0128
X-21916	0.0082	0.0133
AQ-55	0.0077	0.0113
E–MAA	0.0117	0.0259

Table 3. Atomic Coordinates for Cadmium Diacetate Dihydrate[11]

X (Å)	*Y* (Å)	*Z* (Å)	Cd–atom dist (Å)	atom type
0	0	0	0	Cd
0.9898	−2.055	0.2398	2.2935	O
−0.3224	−0.2622	2.2583	2.2962	O
0.0182	1.7725	−1.4645	2.2993	O
−1.7302	−0.9822	−1.1607	2.3034	O
1.8657	1.0716	0.8813	2.3251	O
−2.428	0.7641	−0.0275	2.5455	O
1.3409	−1.3184	−1.7917	2.5974	O
−2.6548	−0.1919	−0.8116	2.7827	C
1.4564	−2.229	−0.9356	2.8223	C
−0.438	0.6484	3.1145	3.2112	C
−1.1149	1.962	2.8075	3.602	C
0.0287	0.4744	−3.8102	3.8398	O
2.7486	−0.5984	2.8893	4.0325	O
1.917	3.6153	−0.9623	4.2038	O
−0.8473	−2.6522	−3.1687	4.2182	O
−4.0513	−0.4542	−1.2952	4.2775	C
0.0287	0.4744	4.2898	4.316	O
2.1334	−3.5426	−1.2425	4.318	C
1.0002	−3.3531	2.5855	4.3507	O
1.0185	−1.5806	4.05	4.4652	Cd
1.0185	−1.5806	−4.05	4.4652	Cd

Figure 2 suggests that either the number of oxygens in the first shell decreased or the Debye–Waller factor increased for the E–MAA ionomer relative to the sulfonate ionomer. Since the drop in the first-shell height is roughly 20%, the change in peak heights supports a change in coordination number from 6 to 5 in the first shell if no other changes occurred. Qualitatively, this change is confirmed by the small-molecule crystal structure analogue, since both anhydrous cadmium formate[10] and cadmium acetate dihydrate[11] have fivefold oxygen coordination centered around a distance of about 2.30 Å. The former structure is clearly not the structure of the materials in this study, since the bulky polymer chain precludes the tightly packed oxo-bridged formate structure. However, the polymer chain could be accommodated in an arrangement where the local structure around the cation is identical to that of the cadmium acetate dihydrate, and hence its structure was used to simulate the structure of the E–MAA ionomer. The atomic coordinates of cadmium acetate dihydrate are shown in Table 3.

FEFF6 simulations using the crystal structure of cadmium acetate dihydrate are compared to the experi-

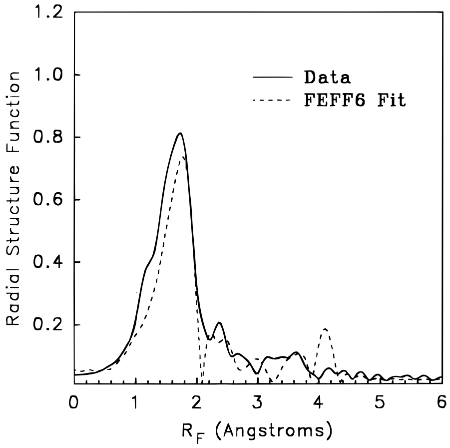

Figure 5. FEFF simulation for E−MAA using the atomic positions derived from cadmium acetate dihydrate. The Debye−Waller factor for the first shell was 0.007 Å^2, while the remaining Debye−Waller factors were arbitrarily set to 0.007 Å^2.

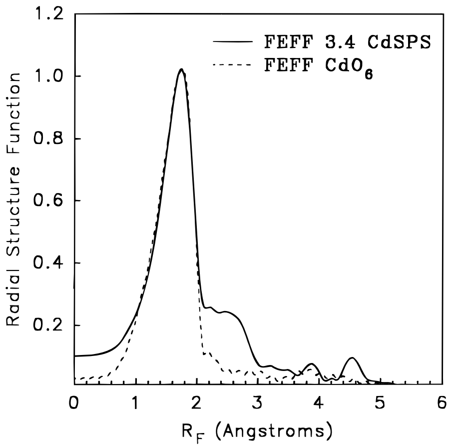

Figure 6. FEFF simulation shown in Figure 4 compared to a simulation with cadmium octahedrally coordinated to oxygen at a distance of 2.30 Å. The latter has been arbitrarily scaled so that the peak heights of the first shell match; in actuality, the peak height of the latter is roughly 25% greater than the former. The Debye−Waller factors for the latter were arbitrarily set to 0.007 Å^2.

mental EXAFS pattern of the E−MAA ionomer in Figure 5. The same Debye−Waller factor was used for the five oxygen atoms at roughly 2.30 Å and the two oxygen atoms at roughly 2.55 Å. The Debye−Waller factor for the remaining atoms was arbitrarily fixed at 0.007 Å^2. The fit is quite poor; the simulation significantly underestimates the height of the first-shell peak. The fact that the simulation RSF peak height did not scale linearly with the number of first-shell oxygen atoms was almost certainly due to destructive interference between backscattered waves of the first nearest neighbor oxygen atoms and atoms from other shells. The efficiency of destructive interference effects can be highly dependent on the exact atomic positions as demonstrated in ref 3; a small error in the positions listed in Table 3 or a small error in the calculation by the software could lead to significant changes in first-shell peak height. One would expect that the two oxygen atoms at 2.55 Å might be the cause of this destructive interference; however, arbitrarily increasing the Cd−O distance by 0.05 Å did not affect the simulation significantly. At this time, the source of the destructive interference is not clear.

One thing quite disturbing about the fits in general was the rather high value for the shifts in the edge energy; for the sulfonate ionomers E_0 shifts ranged from 3 to 7 eV. Since E_0 and R are typically highly correlated, these shifts are probably related to the disagreement between the Cd−O distance simulated by FEFF and the actual Cd−O distance as determined by experimental EXAFS patterns for cadmium oxide discussed in ref 3.

Although quantitatively assigning features in shells other than nearest and next-nearest neighbors should be attempted only with great care, the presence of the features does suggest a more complicated structure than if cadmium atoms were completely surrounded by water. Figure 6 shows the FEFF simulation results for oxygen octahedrally coordinated cadmium atom at a distance of 2.30 Å. This simulation should closely resemble the experimental result if water were sixfold coordinated to cadmium, since the next-nearest backscattering atom (hydrogen backscattering is insignificant) would be over 4 Å from the central cadmium atom. The small features at higher R_F in the experimental data are indicative of a more complicated environment than cadmium surrounded just by water. Differences in the feature centered at $R_F = 2.4$ Å for the experimental sulfonate ionomer EXAFS data may be evidence of different water contents, since the effect of small differences in water content would most likely appear in this region of the RSF rather than in the first-shell region.

The well-ordered local environment around the cation is certainly consistent with the fact that ionic aggregates act as very strong cross-links in ionomers. Furthermore, this local environment may provide valuable insight into the thermal stability of the ionic aggregates.[12−14] The very high melting points of the analogue small-molecule ionic compounds is indicative of the high energy barrier which must be overcome to go from an ordered to a disordered state. However, ionomers can be made to flow at high temperatures if enough force is applied, indicating that the aggregates are not truly rigid crystalline materials, although the local structures are similar (if not identical) to the rigid crystals. EXAFS does not give any direct information about dynamics and cannot be used to quantify the rigidity or flexibility of a structure. Further, EXAFS is not sensitive to longer range order, which is the defining characteristic of a true crystalline material, and, because of the limited aggregate size, this longer range order can extend at most only a couple of nanometers. Just how far this order extends requires a different analytical tool. Differential anomalous scattering is such a tool, and currently studies are underway to determine if the order exists on a length scale larger than a few angstroms.

Summary

The results of this work are consistent with the postulate that the local arrangement of atoms around the transition metal cation in a dried ionomer is very similar to the arrangement which exists in the corresponding small-molecule analogue. For the limited number of materials studied, the identity of the polymer matrix and the ionic level had no effect on the local environment within the ionic aggregates. Simulations suggest that both the carboxylate and sulfonate ionomers had two waters of hydration in the coordination sphere, with the remaining oxygens from the anions. As expected, however, the EXAFS patterns were quite different for the ionomers containing the two different anions. The sulfonate ionomers had six oxygen atoms in the first coordination shell and the structure of the ionomer was successfully modeled using the crystal structure of cadmium methanesulfonate dihydrate, while the crystal structure of cadmium acetate dihydrate was used to model the carboxylate ionomer. The fit of the theory to experiment was not as good in the latter, although small changes in atomic positions would significantly improve the fit.

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