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Relative size of ionic aggregates determined by X-ray absorption spectroscopy

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Abstract

Extended X-ray absorption fine structure (EXAFS) spectra differed slightly with neutralization level in nominally dry ethylene–methacrylic acid copolymer ionomers neutralized with zinc. These small changes in EXAFS spectra were used to infer that decreases in average aggregate size occur with the decreasing neutralization level and that all zinc ions are in aggregates. However, at sufficiently low neutralization levels, EXAFS results indicate some isolated zinc ions were also present. If no water is present, aggregates almost certainly terminate in zinc cations coordinated to two oxygen atoms from bidentate non-chelating carboxylate anions and two oxygen atoms from bidentate chelating carboxylate anions. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Extended X-ray absorption fine structure; Ionomer

1. Introduction

In a recent paper [1], X-ray absorption spectroscopy studies indicated that the arrangement of atoms around zinc in dry ethylene–methacrylic acid (E–MAA) ionomers was similar to the arrangement of atoms in monoclinic anhydrous zinc acetate [2]. This conclusion was based on the essentially exact agreement of the feature in the extended X-ray absorption fine structure (EXAFS) spectra due to nearest-neighbor oxygen atoms coupled with qualitatively similar features due to next-nearest neighbors. As noted in the previous paper, disagreement in the latter was expected, as the three-dimensional crystal structure of monoclinic anhydrous zinc acetate cannot persist at the edges of an ionic aggregate. If the aggregates are not too large, EXAFS patterns should be sensitive to the arrangement of atoms at the edges of aggregates.

Features in EXAFS patterns due to backscattering by second and higher coordination shells were noticeably different for different compositions; however, no basis was available at that time to prove these small differences were not due to statistical uncertainty. Since that paper was submitted, multiple spectra from identical samples have been collected and the error throughout the entire spectral range has been quantified. The error in EXAFS data collected by our laboratory has proven to be extremely small and these variations noticed previously are in fact statistically significant at a high confidence level. This study describes a specific feature in EXAFS patterns of zinc-neutralized E–MAA ionomers, which seems to be sensitive to the average size of aggregates.

Small-angle X-ray scattering (SAXS) and transmission electron microscopy (TEM) have also been used to probe the average size of aggregates. If the scattering angle of the peak in SAXS patterns is a measure of the interparticle separation distance, the aggregates are assumed to be spherical, and the relative amount of phase separation is constant, then the separation distance should scale with ion content to the 1/3 power if the average aggregate size is constant with ion content. Studies of amorphous ionomers where the placement of ionic groups are random have invariably shown that the scaling exponent is less than 1/3 [3], consistent with increases in aggregate size with increasing ion content.

TEM studies are difficult to perform on ionomers because of the difficulty in obtaining a sufficiently thin sample and the possibility of carbon grain artifacts as pointed out by Handlin et al. [4]. A recent TEM study by Winey et al. on zinc E–MAA ionomers appears to be free of these artifacts [5]. Two samples were examined; one with 22% neutralization and one with 55% neutralization. These researchers found that the average aggregate size did not change with neutralization level, unlike what was found in this work. However, TEM might have trouble correctly imaging small aggregates, and the average aggregate size can appear to be constant if a significant number of small aggregates are

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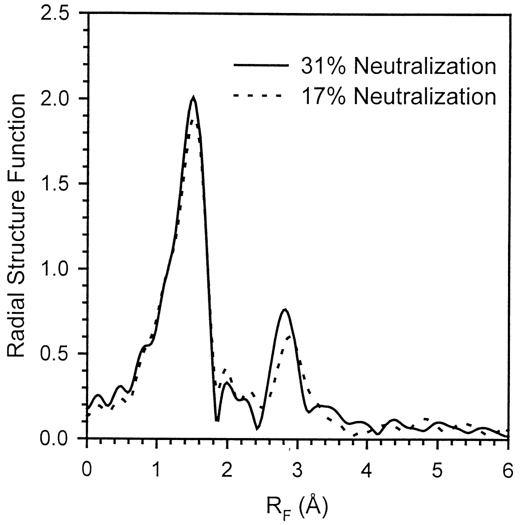

Fig. 1. Radial structure functions for two E–MAA ionomers. The 17% neutralization materials was made from a copolymer containing 10 wt% methacrylic acid repeat units.

not counted. Also, the sample preparation techniques in this current manuscript and in the Winey paper are significantly different, which may be the source of the disagreement.

2. Experimental

All samples were supplied by DuPont Inc. Except where noted, these copolymers contained 11 wt% methacrylic acid repeat unit. Samples were neutralized with a laboratory extruder using varying amounts of zinc oxide and then compression molded into appropriately sized discs. Percent neutralization was based on the amount of carboxylate groups in the system, i.e. 100% neutralization meant that all carboxylate groups were neutralized with no excess zinc present. Percent neutralization was determined using electron microprobe analysis (EMPA), which has an error of approximately 5% based on duplicate measurements. To ensure the accuracy of EMPA measurements, one sample was also measured commercially by Galbraith Labs using inductively coupled plasma. Results from the two methods were identical within the respective error of the measurements. Samples were dried at 70°C in a vacuum oven for one week; drying at 100°C did not remove more water. Although the above facts suggest that the samples were completely dry, this result is not definitive. EXAFS measurements were performed at the Stanford Synchrotron Laboratory on Beamline 2-3 and the measurement temperature was 20 K. Further details about the samples, measurement and data reduction procedures can be found in the previous publication [1].

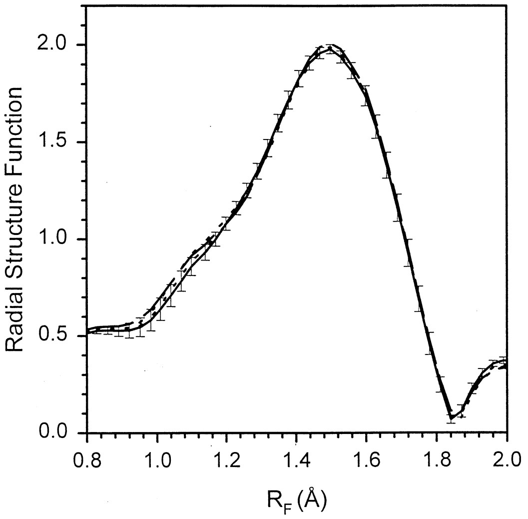

Fig. 2. Radial structure function showing the feature primarily due to backscattering by nearest-neighbor oxygen atoms. Clearly no significant differences in these spectra exist.

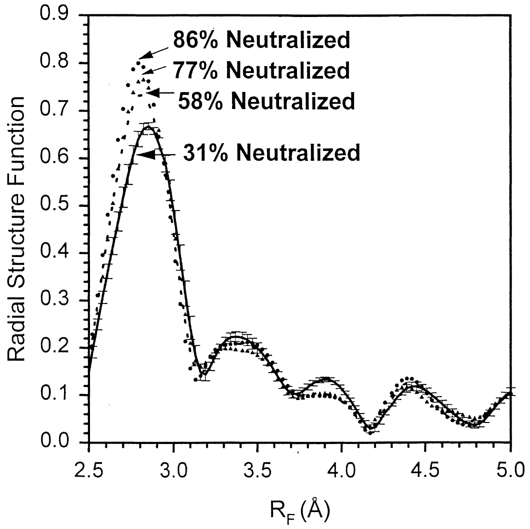

Fig. 3. Radial structure function showing the feature primarily because of backscattering from next-nearest neighbor carboxylate carbon and oxygen atoms. As the neutralization level increases, the peak height increases in magnitude and shifts slightly towards lower R_F.

Errors presented in this paper were calculated from multiple measurements of three different zinc-neutralized E–MAA ionomers similar to the samples presented in this paper. Spectra were collected over a two-year time period during different trips to SSRL. Errors in radial structure functions were calculated by averaging data points with identical X-values.[1] Error bars presented graphically represent the average value of the standard deviation for these three samples; there were no obvious differences in the error from the three different samples. The errors presented in this paper have the same functional dependence and slightly

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[1] Data points having the same X-value were averaged in R-space because error bars are simple to calculate and have clear meaning. However, data should only be averaged in R-space if the radial structure functions are identical. In other words, the radial structure function calculated by averaging radial structure functions from two different compounds is meaningless. EXAFS data from different local environments can be linearly combined, but this mathematical operation must be carried out in k-space not in R-space.

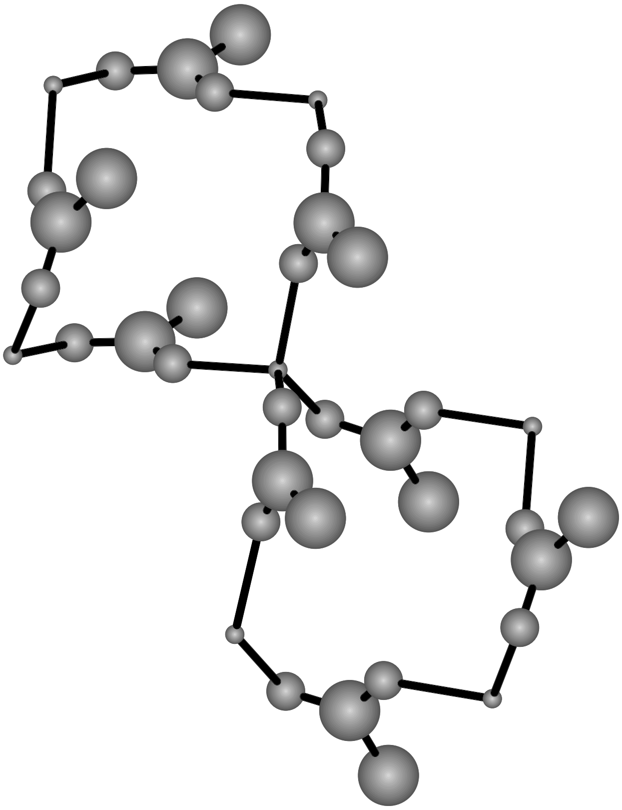

Fig. 4. One possible aggregate structure using atomic positions from crystal structure of monoclinic anhydrous zinc acetate. Small circles represent zinc, medium circles represent oxygen and large circles represent carbon. The carbon atoms with only one bond are polymer backbone carbon atoms. All zinc atoms are either two-fold or four-fold coordinated to carboxylate oxygens. This structure has one interior zinc atom and six edge zinc atoms.

lower magnitude compared to the error presented for PtO_2 by Vaarkamp [6].

3. Results and discussion

Fig. 1 shows an EXAFS pattern for a sample 31% neutralized with zinc and a sample 17% neutralized with zinc. Two large peaks are present; a peak centered at roughly $R_F = 1.5$ Å due to four oxygen atoms at an average distance of approximately 1.96 Å from zinc and a second peak centered at approximately $R_F = 2.9$ Å. This latter feature is primarily a result of backscattering from the carboxylate carbon atom; however the carbon atom attached to the carboxylate atom as well as another carboxylate oxygen atom also contribute to this feature. Fig. 2 represents an enlargement of the peak due entirely to first-shell carboxylate oxygen coordination showing samples with neutralization levels greater than 31%. The second peak is shown in Fig. 3.

Fig. 2 demonstrates that absolutely no change occurs in the first-shell peak with neutralization level as presented previously [1]. However, Fig. 3 presents a very different picture; the height and position of the second-shell peak shifts in a consistent manner with percent neutralization. Changes are very slight at even higher R_F, although a statistically significant difference seems to exist at about $R_F = 4$.

There are three possible interpretations for this difference. The first is that as the neutralization level increases, a higher percentage of ions are found in aggregates. If this assignment is correct, Fig. 2 means that all four first-shell oxygen distances must be essentially identical for aggregated and isolated zinc atoms. This agreement, although not necessarily untrue, is highly unlikely. If all zinc ions were in aggregates at some neutralization level, then as the neutralization level drops, some zinc ions must by necessity become isolated. At this point, changes in the first-shell peak at $R_F = 1.5$ Å should be evident. Although one cannot predict when isolated ions should first appear without a detailed model, changes in the first-shell peak clearly occur at the 17% neutralization level as shown in Fig. 1. The only logical reason for this change is the emergence of isolated zinc atoms. The overall similarity between the first-shell peaks indicates that isolated ions are also four-fold coordinated to oxygen, which was predictable as two carboxylate groups should be chelated to zinc in the absence of water. However, Fig. 1 indicates that individual zinc–oxygen distances are slightly different for isolated and aggregated zinc atoms. Hence, the behavior in Fig. 3 is not because of a change in the distribution of ions inside and outside of aggregates, rather the behavior of Fig. 1 is.

A second possible interpretation of the behavior in Fig. 3 is that the number of unneutralized methacrylic acid groups in close proximity to zinc ions differs. The driving force for this difference would not be aggregate size, but rather the decrease in the number of methacrylic acid groups available for such association. Without any other evidence to the contrary, this supposition is entirely reasonable. However, both IR experiments [7] and rheological experiments [8] indicate that the methacrylic acid groups are not associated with the zinc ion.

The third, and I believe, the correct interpretation of Fig. 3 is that the aggregates become larger with increasing neutralization level. If the average aggregate size is altered, then Fig. 2 indicates that the first-shell zinc–oxygen coordination bonds at the edges of the aggregate are identical to those in the interior; not necessarily expected but not surprising either. If aggregates do differ in size, then features in EXAFS spectra corresponding to the second coordination shell should be different. A reasonable structure of an aggregate based on the crystal structure of monoclinic anhydrous zinc acetate, with almost the same volume as a 1 nm diameter sphere is shown in Fig. 4. Only one out of seven zinc atoms are in the interior of the structure while the remaining six zinc atoms are at the edges of the aggregate. For reasonable structures having the same volume as a 2 nm diameter sphere, between 3/5 and 4/5 of all zinc atoms will be interior atoms depending on the aspect ratio of the aggregate. Water absorption experiments

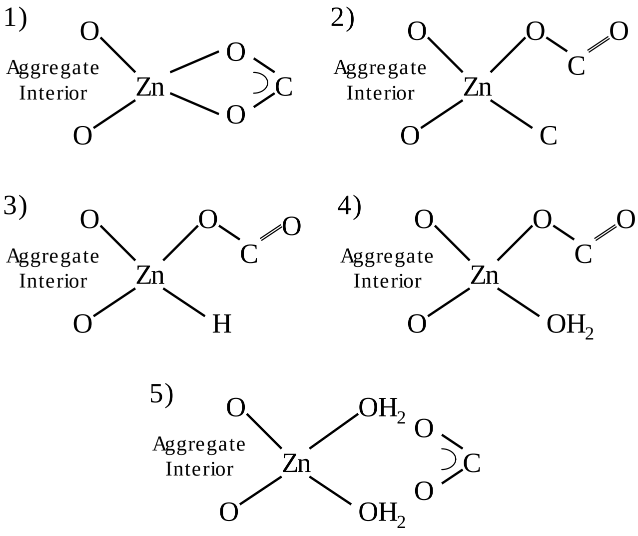

Fig. 5. Five possibilities for structures at the edges of an aggregate.

described elsewhere indicate that water absorbs at aggregate edges and that the amount of water absorbed decreases with increasing neutralization level; consistent with the aggregates becoming larger with increasing neutralization level [9].

If the arrangement of atoms inside aggregates is that of monoclinic anhydrous zinc acetate, zinc atoms at the edges of aggregates must have two oxygen atoms from interior carboxylate anions to supply one negative charge.[2] For the two coordination bonds pointing away from the aggregate interior, one of five possibilities could occur as represented in Fig. 5. All possibilities involve one carboxylate anion in order to maintain charge neutrality.

The first possibility (Fig. 5a) is that the outer carboxylate anion is chelated to the zinc cation. To have this structure, either the O–Zn–O or O–C–O bond angle must be significantly distorted, or the O–C–O bond lengths must increase by almost 50%. All examples of chelating carboxylate groups in small molecule compounds have the O–Zn–O bond angle as approximately 60° with no significant changes in the O–C–O bond. However, to my knowledge, all chelating carboxylate anions occur in six-fold coordinated zinc while in these ionomers only four-fold coordinated zinc is present. This fact does not necessarily mean the chelating structure does not occur in ionomers, particularly because the significant thermodynamic interactions inherent to ionomers do not generally exist in small molecules.

Two possibilities (Fig. 5b and c) can most certainly be rejected based on EXAFS results alone. If the outer carboxylate anion is monodentate instead of bidentate, then the coordination shell could remain unfilled, or could be filled by either carbon or hydrogen. These two possibilities are not supported by the EXAFS spectra, because changes in the sizes of aggregates would certainly lead to changes in the first coordination shell. The fourth and fifth possibilities (Fig. 5d and e) are that even in the fully dried material, water occupies one or two coordination sites. Structures in Fig. 5d and e cannot be eliminated as the dry ionomers might not have been truly devoid of water.

4. Summary

Small changes in EXAFS spectra of zinc-neutralized ethylene—methacrylic acid copolymer ionomers were used to infer that the average aggregate size increases with increasing ion content. Also, aggregate edges most likely consist primarily of chelated carboxylate atoms as shown in Fig. 5a.

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[2] Although it is certainly reasonable to draw structures having three or one oxygens from bidentate, non-chelating interior oxygen atoms, one is left with the intractable problem of isolated carboxylate groups satisfying half-charges.