Infrared and XAFS Study on Internal Structural Change of Ion Aggregate in a Zinc Salt of Poly(ethylene-*co*-methacrylic acid) Ionomer on Water Absorption

Tsutomu Ishioka* and Mamoru Shimizu

Department of Chemistry, Faculty of Science, Toyama University, Gofuku, Toyama 930-8555, Japan

Iwao Watanabe, Shigehiro Kawauchi, and Makoto Harada

Department of Chemistry, Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043, Japan

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ABSTRACT: The internal structural change of an ion aggregate in a zinc salt of poly(ethylene-*co*-methacrylic acid) ionomer on the water absorption−desorption process was investigated by infrared and XAFS spectroscopies. In the infrared carboxylate antisymmetric stretch region, a prominent spectral change was found. In a wet state, the singlet at 1584 cm^{-1} appeared, while in a dry state the triplet at 1537, 1554, and 1625 cm^{-1} was observed. The spectral change was reversible with respect to the water content. From the XAFS analysis, the Zn−O distance and the coordination number were evaluated as 1.95 Å and 4, respectively, in both the wet and dry states. The coordination form of the carboxylate groups around the zinc atom was considered as the bridging bidentate form in the two states. The large infrared spectral change was ascribed to a little reversible geometrical distortion of the tetrahedral coordination structure in the ion aggregate.

Introduction

A series of copolymers of ethylene (E) and methacrylic acid (MA), where the MA units are partially of fully neutralized with such a metal cation as Na or Zn, are known under the trade name of Surlyn of E. I. du Pont de Nemours and Co., Inc., as an ionomer. In a bulk sample of the ionomer, the ionic groups tend to gather and form ion aggregates on neutralization. The aggregates act as ionic cross-linking points and enhance mechanical properties of the ionomer.[1] The molecular level structure of the ion aggregate has been studied by various experimental methods. Eisenberg postulated that there are two types of ion aggregates in some ionomers.[2−4] At low ion concentration below 5−6 mol %, aggregation of a few ionic units called a multiplet is formed. The multiplet consists of only ionic groups and does not contain hydrocarbon chains. When the ion concentration becomes sufficiently high above 5−6 mol %, association of the multiplet occurs and forms a cluster where the constituents are separated from each other by a nonionic matrix.

To elucidate the internal structure of a multiplet or ion cluster, various spectroscopic studies have been carried out. Ion concentration dependence of far-infrared spectra[5,6] and low-frequency Raman spectra[7−9] in polystyrene-based ionomers was investigated, and some characteristic bands were assigned to the translational vibrations of the cation in anionic electrostatic field in either a multiplet or ion cluster. As for the vibrations of the anionic groups, the carboxylate antisymmetric stretch ν_a(COO) mode was found to be sensitive to the amount of hydration and the coordination structure. Brozoski et al. investigated the infrared spectra of E−MA ionomers with various water contents.[10−13] In a dry state, splitting of the ν_a(COO) band was observed for Na, Mg, Ca, Sr, and Ba salts but not for K, Cs, and Zn salts. The split was considered to be indicative of the existence of a locally ordered structure, i.e., multiplet. Several ν_a(COO) bands were tentatively assigned to those of a multiplet or cluster. They also studied the temperature dependence of the infrared bands due to the C−O stretch of the carbonyl and carboxylate groups for a partially neutralized Zn salt of E−MA ionomer.[14] With an increase in temperature, the three carboxylate stretching bands at 1620, 1565, and 1536 cm^{-1} increased in intensity, while the band at 1585 cm^{-1} decreased. They interpreted that this was caused by the change in the coordination structure of the carboxylate groups around the zinc atom and assigned the 1620 cm^{-1} band to the zinc acid salt, the 1565 and 1536 cm^{-1} bands to hexacoordinated zinc carboxylate, and the 1585 cm^{-1} band to tetracoordinated zinc carboxylate.

We have also observed the same splitting of the carboxylate antisymmetric stretch band for a partially neutralized Zn salt of an E−MA ionomer with an increase in temperature,[15] but the spectral change was not reversible with respect to the temperature. Thereafter, we have found that the spectral change was essentially induced by the change in water content, not by the change in temperature. The spectral change occurred even at a low temperature of 40 °C.[16] Structural studies of the ion aggregate are somewhat difficult, since the usual wide-angle X-ray scattering technique for crystals is not applicable to it. Extended X-ray absorption fine structure (EXAFS) or X-ray absorption fine structure (XAFS) is a useful method to study the structure around the metal atom in amorphous material such as E−MA ionomers.[17−21] In this study, to characterize internal structure of the ion aggregate, we discuss the infrared and XAFS spectral change of a zinc salt of an E−MA ionomer on the moisture absorption−desorption process.

Experimental Section

The zinc salt of the E−MA ionomer (referred to E-MA-Zn, Surlyn 472) was purchased from Scientific Polymer Products.

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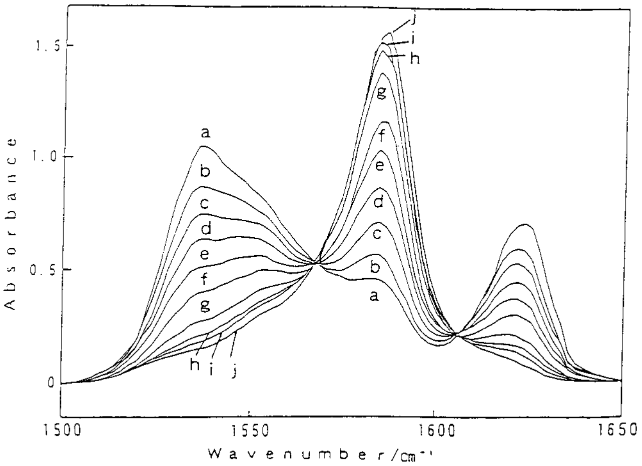

Figure 1. Infrared spectral change in the carboxylate antisymmetric stretch region of E−MA−Zn ionomer at room temperature at various water contents of (a) 0.02, (b) 0.04, (c) 0.06, (d) 0.08, (e) 0.10, (f) 0.13, (g) 0.15, (h) 0.19, (i) 0.22, and (j) 0.28 wt %.

The acidified sample was prepared by dissolving E−MA−Zn in refluxing tetrahydrofuran (THF) containing a stoichiometric amount of hydrochloric acid. The acidified polymer was purified by reprecipitation with methanol from THF solution and dried at 50 °C in vacuo for 24 h. The content of the methacrylic acid comonomer unit was determined by elementary analysis as 5.8 mol % from the total amount of C and 5.3 mol % from the C/H ratio. The degree of neutralization of the E−MA−Zn sample was estimated as 46.8 mol % from atomic absorption analysis for Zn. Film specimens were prepared by melting with a compression molding at 150 °C and 200 kgf/cm^2 and quenching in liquid N_2.

Water absorption−desorption procedures were carried out in a glass vessel which was immersed in a water bath kept at 60 ± 1 °C. The absorption−desorption equilibrium was achieved over 30 h. The amount of water absorbed by the specimens was weighed in an open state by using an electric analytical balance (Sartorius 1712 MP8) with the sensitivity of 10^{-5} g.

Infrared spectra were measured by a JASCO IR-810 spectrophotometer at room temperature in an open state. The weight loss or gain of the sample during the measurement was 0.03 wt % in average.

The zinc K-edge absorption measurements were performed at BL-10B of the photon Factory of the High Energy Accelerator Organization in Tsukuba in which the X-ray beam was monochromatized by a Si(311) channel-cut-crystal monochromator. X-ray transmission spectra were obtained by using a polyethylene pouch as a sample cell at room temperature. The ionomer specimens having different water contents were prepared by the same method for the infrared measurements. The XAFS measurements were performed within 20 min after transferring the ionomer samples sealed in glass vessels into the polyethylene pouch.

Results

A. Infrared Spectral Change. We have reported a reversible infrared spectral change with respect to the water content in E−MA−Zn in the carboxylate antisymmetric and the carboxylate rocking region with the data points of 4.[22] Here, we reexamined the spectral change having the data points of 10 and revised the parameters. We summarize the results. Figure 1 shows the infrared spectral change in the carboxylate antisymmetric stretch region (1500−1650 cm^{-1}) on the water absorption−desorption process at a constant temperature of 60 °C. As the water contents increased from (a) 0.02 to (j) 0.28 wt %, the 1584 cm^{-1} band increased its intensity and the 1622, 1554, and 1537 cm^{-1} bands decreased their intensities parallel with the isosbestic points. This spectral change occurred reversibly with respect to the water content even at 40 °C. It is noted that the spectral change was observed at a constant temperature, and no spectral change was observed in the carbonyl stretch region (1650−1800 cm^{-1}) of the carboxylic acid groups. This indicates two conclusions: (1) the spectral change in the carboxylate antisymmetric region may be not due to the coordination structural change around the zinc atom in which a somewhat large enthalpy change is needed, and (2) the carboxylate spectral change is independent of the carboxylic acid groups. The infrared spectral curves were separated into four bands by assuming a Gaussian + Lorentzian function for each band. The intensity function $I(\nu)$ at the wavenumber ν was expressed as

$$I(\nu) = h_1 \exp\{-\ln 2[(\nu - \nu_0)/\sigma]^2\} + h_2\sigma^2/[(\nu - \nu_0)^2 + \sigma^2] \tag{1}$$

where ν_0 is the peak position. The Gaussian and Lorentzian components had the peak heights of h_1 and h_2, respectively, which were assumed to be 1:1. The two components were postulated to have the same half-width σ. The relative heights (h_2) of the 1537, 1554, and 1625 cm^{-1} bands were fixed at 9:8:7. The ratio was confirmed to remain constant regardless of the water contents. Resultant spectral changes are shown in Figure 2. Parameters obtained are summarized in Table 1. Hence, the triplet at 1537, 1554, and 1625 cm^{-1} is ascribed to a specific structure of the carboxylate groups in the dry state and the singlet at 1584 cm^{-1} to a moistened state.

By using the relative integrated intensities of the triplet and the singlet, the equilibrium between the two states is considered. The integrated intensities of the dry and wet states are denoted by K_{dry} and K_{wet}, respectively. If the thickness and the density of the film are kept constant on the water absorption−desorption process, K_{dry} is expressed as

$$K_{\mathrm{dry}} = \epsilon_{\mathrm{dry}} x_{\mathrm{dry}} \tag{2}$$

where ϵ_{dry} is the integrated molar absorption coefficient of the triplet at 1537, 1554, and 1625 cm^{-1} and x_{dry} is the molar fraction of the carboxylate groups in the dry state. Similarly for the wet state

$$K_{\mathrm{wet}} = \epsilon_{\mathrm{wet}}(1 - x_{\mathrm{dry}}) \tag{3}$$

where ϵ_{wet} denoted the molar absorption coefficient of the 1584 cm^{-1} band. From eqs 2 and 3, we obtained an equation as

$$K_{\mathrm{wet}} = \epsilon_{\mathrm{wet}} - K_{\mathrm{dry}}(\epsilon_{\mathrm{wet}}/\epsilon_{\mathrm{dry}}) \tag{4}$$

Hence, K_{wet} vs K_{dry} plot gives a straight line as shown in Figure 3, and its slope gives the ratio of $\epsilon_{\mathrm{wet}}/\epsilon_{\mathrm{dry}}$ as 0.61. With eqs 3 and 4, x_{dry} is expressed as

$$x_{\mathrm{dry}} = 1/(1 + K_{\mathrm{wet}}\epsilon_{\mathrm{dry}}/K_{\mathrm{dry}}\epsilon_{\mathrm{wet}}) \tag{5}$$

x_{dry} for each water content is evaluated as shown in Figure 4. The intercept of the straight line on the negative side of the abscissa is the amount of residual water in the equilibrium dried state. By adding the value of 0.163 × 10^{-4}mol/g to the water content based on the equilibrium dried state, the water content based

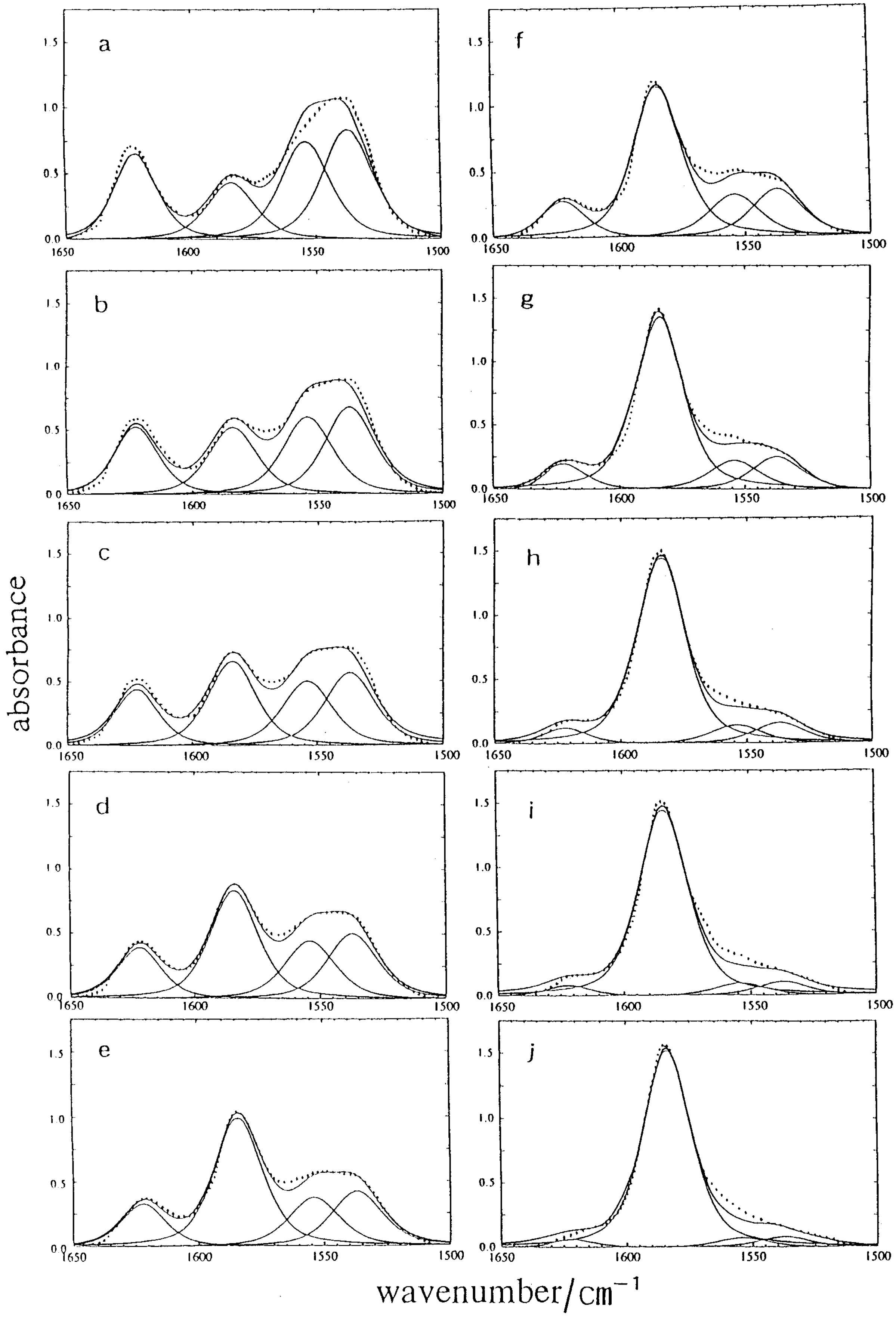

Figure 2. Separated band contours in the carboxylate antisymmetric stretch region of E−MA−Zn at various water contents of (a) 0.02, (b) 0.04, (c) 0.06, (d) 0.08, (e) 0.10, (f) 0.13, (g) 0.15, (h) 0.19, (i) 0.22, and (j) 0.28 wt %: cross, observed; solid line, calculated. The parameters used are listed in Table 1.

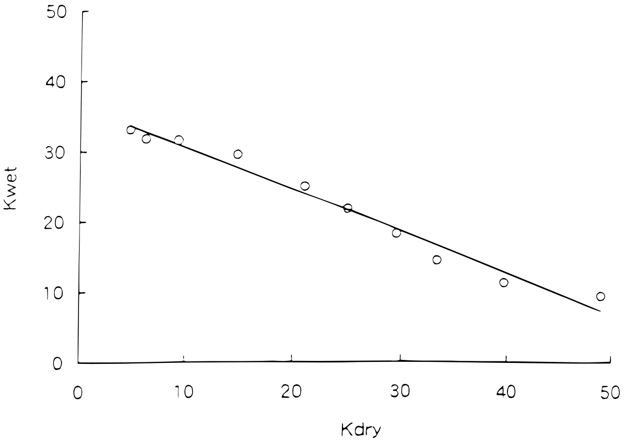

Figure 3. Relation between relative integrated intensities of the triplet (K_{dry} in dry state) and the singlet (K_{wet} in wet state) in the carboxylate antisymmetric stretch region where the straight line was calculated by least-squares.

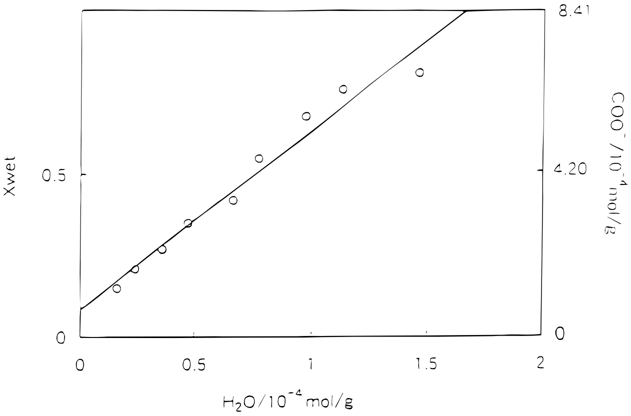

Figure 4. Relation between x_{wet} (the molar fraction of the carboxylate groups in wet state) and the molar amount of water absorbed where the straight line was calculated by least-squares.

Table 1. Peak Heights and the Full Half-Width of the Four Bands at 1537, 1554, 1584, and 1622 cm^{-1} at Various Water Contents

ν/cm^{-1}	1537	1554	1584	1622
σ/cm^{-1}	23.6	23.6	22.4	20.4
H_2O, wt %		$h_1 = h_2$		
0.02	0.384	0.341	0.198	0.298
0.04	0.310	0.276	0.242	0.241
0.06	0.271	0.239	0.318	0.210
0.08	0.232	0.205	0.399	0.180
0.10	0.194	0.171	0.478	0.150
0.13	0.148	0.131	0.544	0.115
0.15	0.087	0.077	0.638	0.067
0.19	0.053	0.047	0.694	0.041
0.22	0.038	0.034	0.700	0.029
0.28	0.026	0.023	0.716	0.020

on the absolutely dried state could be obtained as listed in Table 1. From Figure 4, the ratio of COO/H_2O is evaluated as 4.79 or Zn/H_2O was 2.40. The large difference in the molar absorption coefficients between the dry and wet states ($\epsilon_{wet}/\epsilon_{dry} = 0.61$) is not ascribed to the dielectric field effect[22] but may be ascribed to the vibrational coupling between the COO antisymmetric stretch and the COO rocking mode in which the two modes have the parallel transition dipole moments. Figure 5 shows the spectral change of the COO rocking mode with respect to the water contents. As the water content increased from (a) 0.02 to (j) 0.28 wt %, the intensity of the rocking mode increased. This may compensate for the intensity change in the antisymmetric stretch region.

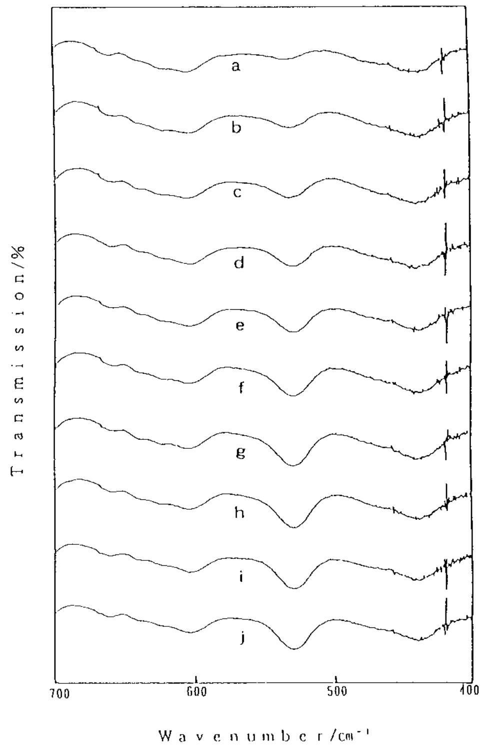

Figure 5. Infrared spectral change in the carboxylate rocking (at 530 cm^{-1}) region of E−MA−Zn at 60 °C at various water contents of (a) 0.02, (b) 0.04, (c) 0.06, (d) 0.08, (e) 0.10, (f) 0.13, (g) 0.15, (h) 0.19, (i) 0.22, and (j) 0.28 wt %.

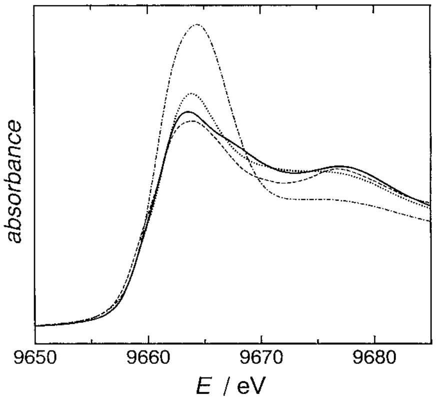

Figure 6. Zn K-edge X-ray absorption near-edge spectra (XANES) for E−MA−Zn ionomer films in wet (dotted line) and dry (solid line) states. Those for 0.1 M zinc(II) ion in water (dash−dotted line) and anhydrous zinc acetate (dashed line) are included for comparison purposes.

B. XAFS Spectral Change. From the infrared spectral change with respect to the water content in E−MA−Zn ionomer, the two structural components ascribed to the wet and dry states were confirmed in the ion aggregate. The infrared spectral change was suggested not to be due to the coordination structural change or the acid salt structural change. Here, we carried out a XAFS experiment for the wet and dry states and examined the change in the coordination structure.

The EXAFS analysis procedures have been reported in detail[23] and thus will not be given here.

In Figure 6 the X-ray absorption near-edge spectra (XANES) for E-MA-Zn ionomer films in the wet (dotted line) and dry (solid line) states are compared to those

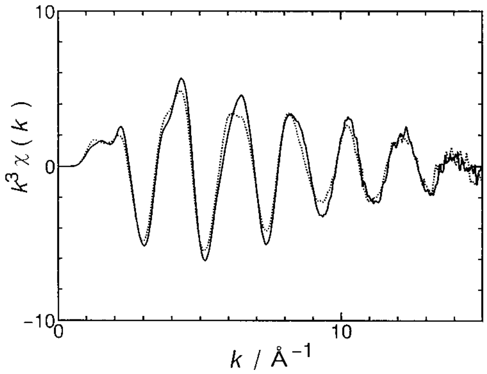

Figure 7. Zn K-edge EXAFS $k^3\chi(k)$ spectra of E−MA−Zn in wet (dotted line) and dry (solid line) states.

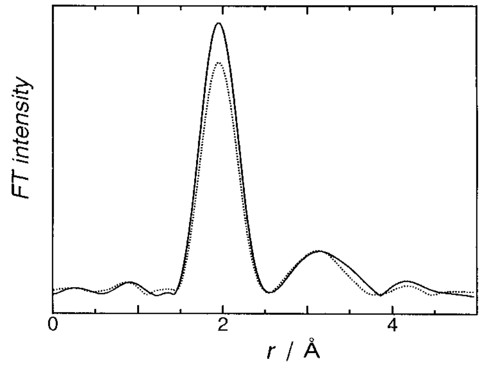

Figure 8. Zn K-edge EXAFS FT spectra of E−MA−Zn in wet (dotted line) and dry (solid line) states.

for the zinc(II) ion in water and anhydrous zinc acetate (dashed line). The coordination structures of zinc ions in aqueous solution and zinc acetate are octahedral and tetrahedral, respectively, and since it is known that the white line intensity increases with the coordination number of zinc ions,[19] the relative intensities of the spectra in Figure 6 indicate that zinc ions in the ionomer films have coordination numbers of around 4.

The coordination structures of zinc ions can be more precisely determined by the EXAFS analysis. The EXAFS oscillation spectra are extracted for ionomer samples as shown in Figure 7. They are Fourier transformed to show radial distribution functions in Figure 8. The FT calculations were performed using the DFT method, and in the calculations the theoretical parameters of phase shift and backscattering amplitude for Zn (absorber) and oxygen (scatterer) were included; thus, the first peaks in Figure 8 appear at the correct position. There clearly exist second peaks at around 3.2 Å in the FT spectra. In the present curve-fitting analysis, two-shell model calculations were performed on the back-transformed χ spectra from the r-space data over the first and the second peaks, i.e., 1.49−3.86 Å.

The variable parameters in the curve-fitting calculation are r, the Debye−Waller-like factor σ, the amplitude factor B ($B = SN$), where S is the amplitude reduction factor, and the absorption-edge shift ΔE_0. The backscattering amplitude $F(k)$ and the phase shift $\phi(k)$ are from the tables by Teo and Lee[24,25] and McKale et al.[26] The coordination numbers N were determined by using the data for zinc acetate as a standard for which $N = 4.0$. The results by the curve-fitting calculations are listed in Table 2.

From the curve-fitting analysis, zinc ions in both dry and wet ionomers are concluded to have the same Zn−O distance of 1.95 Å and the coordination number of 4. Hence, there is no coordination structural change in the water absorption−desorption process in E−MA−Zn. The short distances of 1.95 Å and the small white line intensities in the XANES in Figure 6 also are in excellent accord with the tetrahedral coordination structure of zinc ions.

Table 2. Fitting Parameters of XAFS Analysis for E−MA−Zn in Dry and Wet States

sample	shell	r/Å	N	σ/Å	ΔE_0/e
E−MA−Zn dry	1(O)	1.95	4.2	0.051	8.20
	2(O)	3.28	3.4	0.095	8.20
E−MA−Zn wet	1(O)	1.96	4.1	0.057	6.65
	2(O)	3.22	2.4	0.075	6.65
0.1 M Zn^{2+} in water	1(O)	2.07	6.4	0.083	4.66
$Zn(CH_3COO)_2$	1(O)	1.96	4.0[a]	0.053	7.02

[a] The data from $Zn(CH_3COO)_2$ were used to determine the coordination numbers N for other samples.

We have attempted to identify the elements that produce the second peaks in the FT spectra. The curve-fitting calculations, however, did not give a meaningful difference in the fit when the parameters for carbon or zinc as the backscatterer were used instead of those for oxygen. Therefore, is it possible that either carbon or oxygen of the COO group or even zinc ions are located at around 3.2 Å from the zinc ions in ionomers.

Discussion

First, we discuss the coordination structure around the zinc atom in E−MA−Zn in the dry and wet states where no change in the coordinate structure was confirmed. To estimate the structure, we have made precise studies on the relation between the vibrational spectra and the coordination forms for zinc acetate dihydrate and anhydrous zinc acetate. The zinc acetate dihydrate has the monoclinic crystal structure with the cell dimensions of $a = 14.394(3)$, $b = 5.330(2)$, $c = 10.962(3)$ Å and $\beta = 99.88(2)°$ with $Z = 4$.[27] The molecule has the 6-coordination structure and 2-fold symmetry axis. The Zn−O's (carboxylate) distances are 2.179(4) and 2.189(5) Å, and the Zn−OH_2 distance is 1.987(4) Å. The acetate groups have the chelating bidentate coordination form. On the other hand, the monoclinic anhydrous zinc acetate has the crystal structure with $a = 30.237(2)$, $b = 4.799(1)$, $c = 9.260(1)$ Å and $\beta = 99.49(1)°$ with $Z = 8$.[28] The molecule has the 4-coordination structure. The Zn−O's (carboxylate) distance is 1.957 Å in average. The acetate groups have bridging bidentate coordination forms in a syn−anti arrangement. We have made normal-mode analyses for the two compounds and found that the vibrational frequencies of the carboxylate modes of the antisymmetric and symmetric stretches and the bending and the out-of-plane bending closely coincided each other within 10 cm^{-1} between the two zinc acetates.[29,30] However, the frequencies of the COO rocking mode were different over 50 cm^{-1}; i.e., the chelating bidentate form in the zinc acetate dihydrate gave the frequency at 473 cm^{-1} (Raman), while the bridging bidentate form in anhydrous zinc acetate gave it at 522 (IR) and 526 cm^{-1} (Raman). Hence, the COO rocking mode is the key band to distinguish the two coordination forms. Additionally, the Zn−O (carboxylate) distance is also the key point, since the chelating bidentate has the distance of 2.184 Å in average, while the bridging bidentate has the distance of 1.957 Å. In the case of the E−MA−Zn ionomer, the COO rocking mode was observed at 530 cm^{-1}, and the Zn−O distance was evaluated by the XAFS analysis as 1.95 Å. These indicate that the COO groups in E−MA−Zn have the bridging bidentate structure with the coordination number of 4. It is well-known that the frequency difference between the COO antisymmetric and symmetric stretches is a criterion of the coordination structures.[31] E−MA−Zn has a somewhat large difference of 147 cm^{-1}. This may also indicate that the coordination form is the bridging bidentate. We exclude the possibility of the H_2O coordination to the zinc atom, since the Zn−OH_2 distance in zinc acetate dihydrate is 1.987 Å and is different from the Zn−O distance of 1.95 Å in E-MA-Zn. Several dihydrated compounds of zinc carboxylates have been reported,[27] but they all have the coordination number of 6 and the Zn−OH_2 distance is 1.996 Å in average. The 4-coordinated zinc carboxylates are usually in anhydrous compounds. From our IR analysis, the Zn/H_2O ratio in E−MA−Zn was evaluated as 2.40. This is also different from the ratio of 0.5 of the dihydrates, and water molecules are not coordinated to the zinc atom. Both in the dry and wet states, the COO rocking mode appeared at 530 cm^{-1} and the Zn−O distance was evaluated as 1.95 Å. This indicates that the coordination form does not change during the water absorption−desorption process.

We considered that the spectral change in the COO antisymmetric stretch region was ascribed to slight geometrical distortion in the tetrahedral coordination structure of the COO groups around the zinc atom where the Zn−O distance and the coordination number were retained. A similar slight structural change of the coordination structure has been reported for a carboxylated cadmium ionomer in the anhydrous state.[21] In the dry state of the present ionomer, a slight distortion of the tetrahedral geometry may cause resolving the degenerated spectral frequencies and the large frequency split, although we did not make a quantitative analysis of the frequencies. This kind of split has been also reported for zinc soaps[32,33] and potassium soaps[34,35] in the high-temperature phase where the orientational disorder of the carboxylate groups occurred. The large frequency split in the dry state may be also due to the transition dipole−dipole coupling among the carboxylate groups. The split in the frequency due to the coupling between the carbonyl C═O groups in carboxylic acids has been observed as over 50 cm^{-1}.[36] In the case of the carboxylate group, the coupling is somewhat large because of the large transition dipole moment,[37] causing the large split. The presence of water may relax the distortion and make the coordination structure as an exact tetrahedral form. This exact form results in a singlet in the infrared spectrum, although the detailed role of water is not clarified at the present stage.

In this study, we found an order−disorder structural change of the ionic groups in a zinc salt of the E−MA ionomer on the water absorption−desorption process by infrared spectra. A similar spectral change in the COO antisymmetric stretch region was found for zinc stearate.[38] Zinc stearate has one phase transition at 130 °C. Above the transition point, spectral split was observed and at the same time the ionic conductivity increased. Therefore, we speculate that the ionic conductivity may be affected for E−MA−Zn on the water absorption−desorption process.

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