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(31) The first cumulant $\Gamma(q)/q^2$ can be expressed quite generally as[30]

$$\frac{\Gamma(q)}{q^2} = \frac{k_BT}{\xi}\frac{1}{S(q)}\left\{1 + \frac{\xi}{(2\pi)^3}\int \mathrm{d}^3k\ \bar{T}_{33}(\mathbf{q}-\mathbf{k})[S(k) - 1/x]\right\}$$

where $\bar{T}_{33}(k) = (1-\mu^2)/\eta k^2$ and $S(k) = \sum_{j,m}\nu_j\nu_m \exp(i\mathbf{k}\cdot\mathbf{R}_{jm})/\sum_j\nu_j^2$; $\mu = \mathbf{k}\cdot\hat{\mathbf{q}}$. This form is not restricted to unperturbed Gaussian chains or any particular choice for the Oseen tensor, chain structure, etc. The apparent diffusion coefficient follows from it as

$$D_{\mathrm{app}} = (k_BT/\xi)(\textstyle\sum\nu_j^2/(\sum\nu_j)^2)\left\{1 + (\xi/3\pi^2\eta)\int_0^\infty \mathrm{d}q\ [S(q) - 1/x]\right\}$$

Local Structures in Ionomer Multiplets. A Vibrational Spectroscopic Analysis

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ABSTRACT: The results obtained from a systematic Fourier transform infrared study of the alkali metal, alkaline earth, and zinc salts of an ethylene–methacrylic acid copolymer are presented. The infrared spectra of samples, acquired at elevated temperatures, show spectral features characteristic of local ordered ionic structures commonly referred to as multiplets. From a consideration of the known coordinating tendencies of the different cations, together with a symmetry analysis of the most probable structures, we show that the experimental infrared results of the different ionomers are entirely consistent with the presence of specific local structures.

Introduction

The vibrational spectrum of most polymeric systems can be interpreted in terms of the normal modes of a theoretically isolated chain. The influence of interchain interactions is apparent in only one or two systems, principally because most interchain forces are relatively small and their effect upon the spectrum can be treated as a perturbation. Consequently, infrared and Raman spectroscopy are (for the most part) only sensitive to three-dimensional order in materials where specific strong interactions can be identified. One such class of polymeric materials is ionomers, where the arrangement of charged species should have a major affect on specific normal modes because of the strong electrostatic forces involved.

A number of infrared spectroscopic studies of ionomers have been reported.[1-7] The far-infrared work of Risen and co-workers[3-5] demonstrated the sensitivity of low-frequency vibrations to the nature of the anions and cations involved and the degree of cluster formation. Research in this laboratory[6,7] has concentrated on the bands due to the antisymmetric stretching vibration of carboxylate anions in the spectra of sodium and calcium ionomers of ethylene–methacrylic acid copolymers. These bands coalesce into a single broad entity upon annealing at room temperature for extended periods of time. We previously rationalized such observations in terms of the cluster model of Eisenberg.[8] More recently, we have been forced to reevaluate this interpretation as a result of a study of the effect of water on the carboxylate modes. This work, however, will be presented at another time. Here we will be concerned with results that, at least from a spectroscopic point of view, are more intriguing. In the spectra of melt-quenched and annealed samples a collection of carboxylate modes near 1550 cm^{-1} that are sensitive to thermal history and hence structure can be observed.

In our previous work we interpreted a doublet in the spectrum of calcium ionomers in terms of a splitting due to interactions between pairs of carboxylate groups. The sodium ionomers also gave a collection of bands, but we assigned these modes to multiplet and ion pairs isolated by the quencing process. From the high ground attained by further experimental observations, we can now look back and see that these interpretations were not only naive but more than likely just plain wrong. In fact, one of the referees of our original paper[6] suggested that the collection of bands observed in the spectrum of the sodium ionomer could also be interpreted in terms of a splitting due to interactions between carboxylate groups. At the time we casually dismissed this argument, but in the present paper we will concede that it is indeed correct.

Essentially, the work presented here largely concerns the local arrangement of carboxyl groups in structures termed multiplets by Eisenberg.[8] (Such local structures are probably also found in clusters, but we will address this point separately when we consider the origin of the band broadening previously observed upon annealing.[6]) Our investigation follows two lines. The first is purely experimental. We have obtained the spectra of the ionomers of different cations, principally those of the group 1 and group 2 elements of the periodic table. As we will demonstrate, these results force a major reassessment of our original interpretation. Our second line of arguments is built on questions that arise from theoretical considerations. Based on the coordinating tendencies of specific cations what type of local structures within multiplets would be anticipated? Furthermore, based on the symmetry of such structures what bands or pattern of bands would we predict in the vibrational spectrum? We will show that the spectroscopic predictions of this theoretical approach dovetail neatly with the experimental observations.

Experimental Section

The ethylene–methacrylic acid copolymer used in this study was obtained from E. I. du Pont de Nemours and Company (Surlyn 1650) and was reported to contain 4.1 mol % methacrylic acid. The metal salts were prepared as described in our previous papers by using the pertinent hydroxides.[6,7] To prepare films for infrared analysis each sample was pressed at 40 000 psi and at

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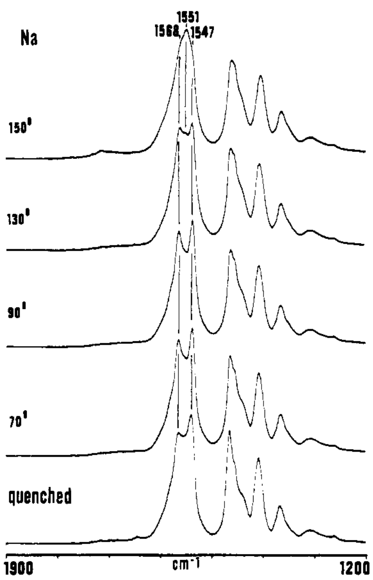

Figure 1. FT IR spectra in the range 1900–1200 cm^{-1} of a completely ionized sodium ionomer at various temperatures.

190 °C several times and quenched in liquid nitrogen after each pressing. These films were thin enough to be within a range where the Beer–Lambert law is obeyed.[9] As in our previous studies we are only concerned with completely ionized ethylene–methacrylic acid copolymers with specific thermal histories. Details of the experimental heating studies are given in the text.

Infrared spectra were obtained on a Digilab FTS-15B spectrometer. Two hundred scans at a resolution of 2 cm^{-1} were signal averaged, and the spectra were stored on a magnetic tape system. Spectra recorded at elevated temperatures were obtained with a SPECAC high-temperature cell and controller mounted in the spectrometer.

Results

In this paper we will consider recently obtained spectra of ionomers containing the alkali metals lithium, potassium, and cesium, the alkaline earth metals magnesium, strontium, and barium, and the transition metal zinc. In order to present the data in a coherent fashion, however, we consider it necessary to review some of the spectral results previously obtained for the sodium and calcium salts.[6,7] We will initially consider the group 1 cations and then subsequently describe the results obtained for the group 2 cations and zinc.

Alkali Metal Ionomers. Figure 1 compares the infrared spectrum of the sodium ionomer of an ethylene–methacrylic acid copolymer quenched from the melt to the spectra of the same sample maintained at various temperatures. Bands in the 1750–1700-cm^{-1} region of the spectrum, attributable to carboxylic acid monomers and dimers,[1] are essentially absent, indicating (practically) complete ionization.[6] Conversely, a collection of bands near 1550 cm^{-1}, characteristic of carboxylate anions, dominates the spectrum. We previously assigned the band near 1568 cm^{-1} to multiplets while the band near 1547 cm^{-1} was assigned to isolated sodium–carboxylate ion pairs. In part, this assignment was based on the *apparent* change in the relative intensities of the 1568/1547-cm^{-1} modes with thermal history. However, a closer examination of the spectra, together with the insight gained from the spectra of other group 1 ionomers that we will consider shortly, suggests an alternative explanation. The 1568/1547-cm^{-1} bands could be a doublet that is the result of some local arrangement of carboxylate anions. The change in the relative intensities of these bands is a result of the appearance of an overlapping mode near 1550 cm^{-1}. This latter band is clearly present in the spectrum of the sample held at 130 °C and dominates the spectrum of the sample held at 150 °C.

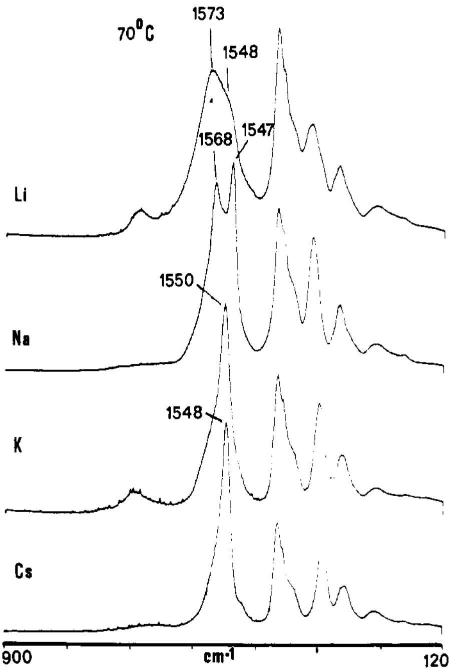

Figure 2. FT IR spectra in the range 1900–1200 cm^{-1} of the completely ionized alkali metal ionomers at 70 °C.

Eisenberg[8] has argued that the formation of clusters depends upon the balance between the elastic forces of the polymer chain and the attractions between small ionic domains termed multiplets. (A simple ion pair is the limiting case of a multiplet.) As the temperature of the sample is raised, the balance between the elastic forces of the chain and the electrostatic attractions between ionic groups is perturbed, thus influencing the distribution of associated states. The band near 1550 cm^{-1}, which increases in intensity with increasing temperature, could therefore be due to simple ion pairs, while the doublet at 1568/1547 is more probably associated with some sort of local structure found in multiplets (and clusters).

Similar temperature studies were performed on all of the ionomers used in this study. The spectra of samples held in the temperature range 70–90 °C were always the sharpest and best defined, probably because such temperatures are high enough to minimize the presence of trace amounts of water (which would hydrate and disrupt ionic structures), but not so high as to favor simple ion pairs over more organized structures. Accordingly, the remaining spectra of group 1 and group 2 ionomers presented here are those obtained from samples held at 70 °C.

The spectra of the lithium, sodium, potassium, and cesium salts are compared in Figure 2. Qualitatively, the spectrum of the lithium salt is similar to that of the sodium ionomer, with a pair of bands near 1573 and 1548 cm^{-1} clearly present. However, the bands are broader and there are additional weak modes near 1590 and 1687 cm^{-1}. In contrast, the spectra of the potassium and cesium salts are of a completely different character. The spectra of both are dominated by a surprisingly sharp single band near 1550 cm^{-1}. Modes near 1675 and 1590 cm^{-1} can again be observed but are relatively weak.

Alkaline Earth Ionomers. We have previously reported temperature and annealing studies of the calcium ionomer,[6,7] but for completeness the spectrum of this salt is compared to those of other group 2 elements in Figure 3. (Attempts to prepare the beryllium ionomer were unsuccessful, so that magnesium is the smallest group 2

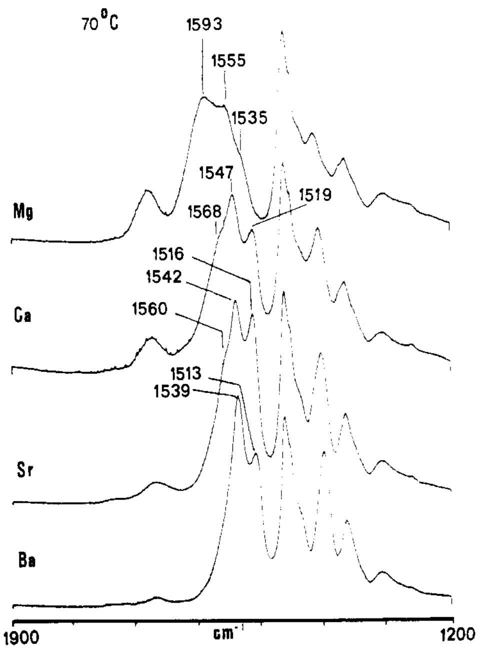

Figure 3. FT IR spectra in the range 1900–1200 cm^{-1} of the completely ionized alkaline earth ionomers at 70 °C.

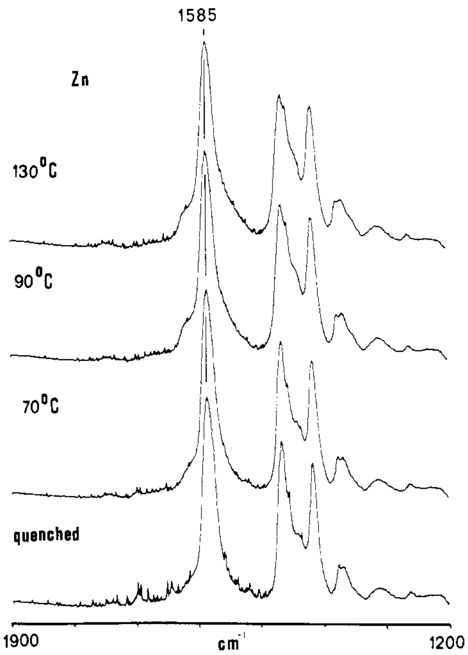

Figure 4. FT IR spectra in the range 1900–1200 cm^{-1} of a completely ionized zinc ionomer at various temperatures.

cation studied.) The spectra of all these samples are characterized by a doublet, at 1539 and 1513 cm^{-1} in the spectrum of the barium salt but at progressively higher frequencies as the size of the cation decreases. The spectrum of the barium salt also has a weak band near 1680 cm^{-1} and a barely perceptible shoulder near 1580 cm^{-1}. These bands increase with decreasing cation size and are prominent in the spectrum of the magnesium salt.

Summary. At this stage it is pertinent to summarize the major trends that we have observed for the group 1 and group 2 cations.

(1) Major differences are observed in the spectra obtained at elevated temperatures for the alkali metal ionomers. The essential features of the lithium and sodium salt spectra are the same. Multiple bands are observed in the asymmetric carboxylate stretching region and there is good evidence for the presence of characteristic doublets. Conversely, in the larger alkali metal cations, potassium and cesium, the spectra are primarily characterized by a single sharp band.

(2) All of the spectra obtained at elevated temperatures for the alkaline earth salts studied exhibit characteristic bands in the asymmetric carboxylate stretching region that are apparently doublets. Two other bands occurring at higher frequencies (e.g., the 1568- and 1680-cm^{-1} bands in the calcium ionomer) are also present in all the alkaline earth ionomers. We have observed that the appearance of the high-frequency shoulder is apparently related to the presence of a mode near 1680 cm^{-1}. When this latter band is prominent, so is a shoulder between 1560 and 1595 cm^{-1} (the precise frequency being dependent upon the counterion).

(3) As we progress in the series from magnesium to barium, the frequencies of the bands in the asymmetric carboxylate stretching region decrease in frequency in a predictable manner with cation mass and size.

Zinc Ionomer. Finally, although it does not fit into our general scheme of examining ionomers of group 1 and group 2 cations, it is important to consider the spectrum of the zinc salt. Zinc salts are commonly used in ionomers of commercial significance. On the basis of a superficial analysis, the doublet appearing in the spectra of the group 2 materials might be considered to be due to pairs of carboxylate anions bridged by divalent cations.[6] However, this leaves the bands in the spectra of the sodium and lithium ionomers to be rationalized in some fashion. Our doubts concerning such an interpretation were deepened by a consideration of the spectrum of the zinc ionomer, presented in Figure 4. Surprisingly, this material is characterized by a single band at 1585 cm^{-1}. There is little change in the spectrum of the zinc ionomer during the temperature studies. In fact, this observation was the final straw that forced us to abandon our original interpretation. We will show that an analysis based on the coordinating tendencies of the cations provides a more satisfactory and complete explanation for the experimental results.

Discussion

The results presented in the previous section raise some important questions. The relatively sharp singlet and doublets observed in the asymmetric carboxylate stretching region of the spectra of the various ionomers suggest the presence of locally ordered ionic structures (multiplets?); in this context, there is one key question that must be addressed: why do certain ionomers exhibit sharp singlets (e.g., the K, Cs, and Zn salts) while others exhibit distinct doublets (e.g., the Na, Ca, Sr, and Ba salts)?

The asymmetric carboxylate stretching vibration is essentially uncoupled from backbone modes. Consequently, in any ordered structure containing a specific number of such interacting groups, we would expect the appearance of infrared bands to be markedly influenced by local symmetry. Thus it is reasonable to perform a symmetry analysis of the "unit cell" of structures that incorporate the most probable arrangements of carboxylate groups and determine the number of active symmetric and asymmetric carboxylate stretching modes.[10] (In this Discussion we will concentrate our attention on the asymmetric modes. The spectral region in which the symmetric modes occur is complicated by overlapping bands associated with the methylene bending vibrations.)

The simplest arrangements of carboxylate groups in ionomers of divalent cations would be as a pair, as we originally postulated for the calcium salt.[6] Figure 5 illustrates two probable structures, a planar arrangement (denoted A) and a configuration where the two carboxylate

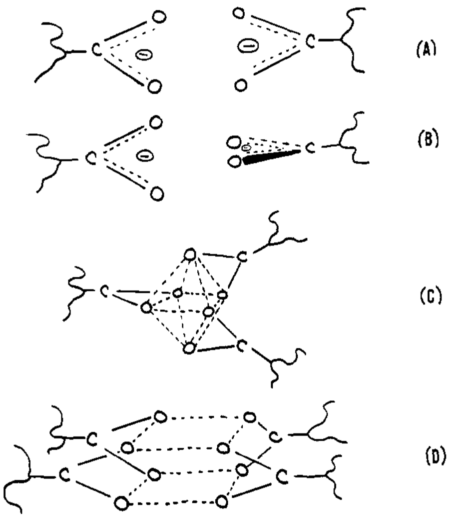

Figure 5. Possible structures for multiplets with coordination numbers of (A) 4, (B) 4, (C) 6, and (D) 8.

anions are at 90° to one another (B). The former has D_{2h} symmetry while the latter belongs to the point group S_4. Using internal coordinates as a basis, one can determine the symmetry species and hence the vibrational activity of the asymmetric modes.[10] For the planar structure, the two asymmetric modes belong to the B_{1g} and B_{2u} symmetry species respectively, but *only* the B_{2u} mode is infrared active. The two asymmetric stretching modes in the S_4 structure (Figure 5B) are doubly degenerate (i.e., have the same frequency), belong to the E irreducible representation, and are both Raman and infrared active. In any event, only *one* discernible infrared band is predicted. Other possible arrangements of the carboxyl groups were analyzed (e.g., structures similar to the planar form where the carboxylate anions are vertically offset above and below the plane), but the result remains the same. For structures involving a single pair of carboxylate anions, a symmetry analysis predicts only one infrared-active asymmetric stretching mode.

On the basis of this somewhat surprising result we decided to extend our symmetry analysis to other possible structures, specifically those that can be postulated on the basis of packing requirements. In a number of previous studies, for example, the seminal theoretical work of Eisenberg,[8] it has been pointed out that the coordinating tendency of the cation could be critical in forming multiplets. The coordination number for simple inorganic structures can be predicted to some extent on the basis of the ratio of the radii of the ions involved, as indicated in Table I. As a first approximation we used the ionic radius of the O^{2-} ion in our calculations together with values for cationic radii listed in standard inorganic texts[11] and obtained the predicted coordination numbers that are also listed in Table I. The experimentally determined coordination numbers of some simple metal oxides are also listed in this table.[11]

In the context of this analysis, it is significant that for the alkali metal cations we predict different coordination numbers for the smaller cations (4 or 6 for lithium and sodium) compared to the larger cations (8 for potassium and cesium). In the case of the alkaline earth cations a similar trend is determined, i.e., a coordination number of 4 or 6 for magnesium and calcium and 8 for strontium and barium. However, it is important to realize that the above calculations are crude and even in simple metal oxides the predicted coordinations numbers do not always correspond to those actually found. For example, a coordination number of 6 is observed for all the alkaline earth oxides (see Table I). For the zinc cation, structures with a coordination number of 4 or 6 are predicted, while a tetrahedral structure with coordination number of 4 is found in zinc oxide.

Table I

radius ratio	coord no.	structure
0.155	3	trigonal
0.225	4	tetrahedral
0.414	4	square planar
0.414	6	octahedral
0.732	8	body-centered cubic

cation	radius ratio (M/O)	coord no. pred	coord no. obsd
Li	0.49	4 or 6	
Na	0.68	4 or 6	
K	0.95	8	
Cs	1.21	8	
Mg	0.46	4 or 6	6
Ca	0.71	4 or 6	6
Sr	0.81	8	6
Ba	0.96	8	6
Zn	0.53	4 or 6	4

Having set the stage, we will now turn our attention to a symmetry analysis of 6- and 8-coordinated structures. On the basis of the packing characteristics of simple ions the structures illustrated in Figure 5 can be considered reasonable analogues for multiplets occurring in certain ionomers. The octahedral structure, which has a coordination number of 6 (i.e., three carboxylate anions) belongs to the symmetry group D_3. The three asymmetric stretching modes are distributed among the A_2 and E species. Both of these modes are infrared active. On the other hand, the body-centered cubic structure, which has a coordination number of 8 (i.e., four carboxylate anions) belongs to the D_{4h} symmetry group. Four asymmetric stretching modes are distributed among the A_{2u}, B_{1u}, and E_g symmetry species. The B_{1u} mode is inactive and the E_g mode is only Raman active, leaving solely the A_{2u} mode as an infrared-active vibration. Surprisingly, of those considered, we predict the presence of more than a single infrared-active asymmetric stretching vibration in only one structure, that with six coordinated oxygen atoms (three carboxylate groups).

In the preceding symmetry analysis we have only considered relatively simple arrangements of ions. More complicated structures are found in various coordination complexes. For example, a trigonal-prismatic structure, which can be considered a distortion of the symmetric, 6-coordinated octahedral structure (Figure 5C), is possible. However, such complexes are often the result of special factors such as the presence of a rigid cage ligand which can force the prismatic arrangement.[11] Furthermore, the types of structures formed by carboxylate ions will be limited sterically, first by the connection of pairs of oxygen atoms to a common carbon atom and second by the attachment of these carbon atoms to polymer chains. Consequently, the formation of highly complex coordination complexes appears to us unlikely.

Let us now return to an examination of our experimental result, using the fresh light of this symmetry analysis. We will first consider the alkali metal ionomers. On the basis of the ratio of ionic radii and known coordinating tendencies, lithium and sodium salts would prefer a coordination number of 6 (although a coordination number of 4 with the oxygen atoms in a square-planar arrangement is also a possibility). In the infrared spectra of the lithium and sodium ionomers (Figures 1 and 2) distinct doublets are observed. This would suggest that the multiplets in the lithium and sodium ionomers form octahedral structures. In contrast, the predicted coordination number for the potassium and cesium salts is 8. Only one infrared-active asymmetric carboxylate stretching vibration is predicted for such structures and that is precisely what is observed in the experimental spectra (Figure 2).

In the experimental spectra of all the alkaline earth ionomers (Mg, Ca, Sr, and Ba; see Figure 3) we observe distinct doublets in the asymmetric carboxylate stretching region, implying a coordination number of 6. Our rough calculations indicate that the magnesium and calcium salts would prefer coordination numbers of 4 (square planar) or 6 while the strontium and barium salts would prefer coordination numbers of 8. However, the experimentally observed coordination numbers of the alkaline earth oxides are identical and have a value of 6.

In contrast to the other ionomers of divalent cations considered in this study, the carboxylate stretching region of the spectrum of the zinc salt is dominated by a single band. On the basis of ionic radii a coordination number of 4 or 6 is predicted, but in zinc oxide a coordination number of 4, with the oxygen atoms arranged tetrahedrally, is observed. A symmetry analysis of this structure predicts the observed singlet.

We realize that this analysis is imperfect for a number of reasons. The radius of the oxygen atoms in the carboxylate anions is probably somewhat smaller than that of the O^{2-} ion; the steric packing factors could differ from those in simple oxides; furthermore, additional cations would have to be packed around or between such structures to achieve electrostatic balance. Nevertheless, there are a number of factors that lead us to believe that this analysis has some validity. For example, the structures found in copper carboxylate salts[12] and salts of various stearates[13-15] correspond to those that form the basis of this analysis. In addition, studies of transition-metal ionomers using ESR (as well as infrared and electron microscopy) indicate the formation of complexes involving more than one cation.[16-19] Ultimately, however, our arguments come to rest on one major consideration. Does the analysis successfully predict the experimental observations? We believe that it does.

Before we summarize the above discussion, we wish to clarify the assignment of the shoulder occurring between 1560 and 1595 cm^{-1} that is evident in most of the ionomer spectra and the band near 1680 cm^{-1}, which is apparently associated with it. Hydrogen-bonded pairs of carboxylate acid groups are characterized by an infrared band near 1700 cm^{-1}, so that a mode near 1680 cm^{-1} would have to be due to a more strongly bound $\mathrm{C{=}O}$ species of some description. We previously proposed a six-membered-ring complex,[6] and this remains a possibility. An alternative assignment, and one that we now prefer since it also explains the shoulder near 1580 cm^{-1}, is to an acid salt structure. These are well-known to occur, for example, in stearates and give spectroscopic results similar to those observed here.[20] The types of structures that are formed in acid salts can lead to very short hydrogen bonds[21] so that we would anticipate a lower frequency for the $\mathrm{C{=}O}$ group. More work will be necessary to fully understand the origins of these bands. The role of water and partial ionization are two factors that are currently being investigated.

Summary and Conclusions

In the infrared spectra of ionomers we observe a pattern of bands in the asymmetric carboxylate stretching region of the spectrum that varies with the nature of the cation. On the basis of the coordinating tendency of each cation various local arrangements of the carboxylate groups can be postulated. A symmetry analysis of these local structures successfully predicts the experimentally observed results.

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Registry No. (Ethylene)·(methacrylic acid) (copolymer) lithium salt, 27135-20-2; (ethylene)·(methacrylic acid) (copolymer) sodium salt, 25608-26-8; (ethylene)·(methacrylic acid) (copolymer) potassium salt, 26376-80-7; (ethylene)·(methacrylic acid) (copolymer) cesium salt, 26834-55-9; (ethylene)·(methacrylic acid) (copolymer) magnesium salt, 75062-18-9; (ethylene)·(methacrylic acid) (copolymer) calcium salt, 26702-73-8; (ethylene)·(methacrylic acid) (copolymer) strontium salt, 88496-05-3; (ethylene)·(methacrylic acid) (copolymer) barium salt, 88496-06-4; (ethylene)·(methacrylic acid) (copolymer) zinc salt, 28516-43-0.

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