Vibrational Study of the Polymer Electrolyte Poly(ethylene oxide)$_6$:LiAsF$_6$

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ABSTRACT: A vibrational study of the polymer electrolyte compound poly(ethylene oxide)$_6$:LiAsF$_6$ is reported. A symmetry-based factor group correlation method is applied to interpret the observed bands. The Raman and infrared spectra of the compound are consistent with the reported crystal structure. The ν_1 mode, which appears at 685 cm^{-1}, identifies the anions as being “spectroscopically free”. Multiple bands in the ν_3 spectral region are interpreted as resulting from the dynamical coupling of the four AsF$_6^-$ anions in the unit cell. The ρ(CH$_2$) region shows multiple bands that arise from the complex conformations of the polymer backbone.

1. Introduction

Polymer electrolytes are of considerable interest due to their potential applications in rechargeable batteries and other electrochemical devices.[1−3] Investigation of cation−polymer and cation−anion interactions is essential to understanding the microscopic mechanism of ionic transport in polymer electrolytes. The study of crystalline phases in certain poly(ethylene oxide)−alkali metal salt systems yields the structures and bonding geometries in these systems[4,5] and provides insight into the local structure of the amorphous phase,[6,7] which is primarily where ionic conductivity occurs.[8,9]

Ionic transport in poly(ethylene oxide)−salt systems is coupled to the segmental motion of the polymer host.[10,11] Although the specific nature of the segmental motion is not known, it is generally considered that segmental motion involves changes in the conformation of the polymer backbone. Analysis of crystalline polymer−salt structures[4,5] and vibrational spectroscopic studies of polymer−salt systems[12−15] show that the conformation of the poly(ethylene oxide), PEO, backbone is altered upon complexation to cations. Ab initio calculations have been used to determine the relative energies of various conformational sequences and model the energetic barriers for the migration of a lithium ion.[16−20] Molecular dynamics simulations have been used to examine the relative populations of various conformational sequences.[21,22]

The extent and nature of ionic association is also a critical factor in the ionic conductivity and transport properties of the electroyte.[23] Vibrational spectroscopy has proven to be a powerful tool to examine the ionic association of the salt anion.[12,24−26] In particular, we consider the determining the vibrational signatures of the crystalline polymer−salt compounds to be crucial to investigating the local structure in amorphous and multiple-phase polymer electrolytes. We have recently studied the crystalline compounds P(EO):NaCF$_3$SO$_3$ and P(EO)$_3$:LiCF$_3$SO$_3$ and have interpreted multiple CF$_3$SO$_3^-$ anion bands as resulting from coupling of the vibrational modes in the crystal.[27]

The structure of the crystalline compound poly(ethylene oxide)$_6$:LiAsF$_6$ (abbreviated P(EO)$_6$:LiAsF$_6$), which was elucidated from X-ray diffraction patterns, has been recently reported.[28] This structure is strikingly different from those of other polymer−salt compounds in that there is no coordination of the lithium ions by the anions. Therefore, it is of interest to examine the local environment of the hexafluoroarsenate anions by vibrational spectroscopy, with the expectation that the AsF$_6^-$ mode frequencies would correspond to those of a “spectroscopically free” anion. A study of the polymer modes in P(EO)$_6$:LiAsF$_6$ furthers our knowledge of the relationship between vibrational frequencies and specific conformational sequences. Mid-infrared and Raman spectra of the P(EO)$_6$:LiAsF$_6$ compound have been recorded, and the vibrational analysis is presented.

2. Experimental Section

PEO, $M_w = 4 \times 10^6$, was obtained from Aldrich and dried under vacuum at 50 °C for 24 h. Thin films were made by casting a solution of PEO in acetonitrile onto Teflon sheets. The P(EO)$_6$:LiAsF$_6$ compound was obtained from Professor Peter Bruce, St. Andrews University. To prepare the sample, dried PEO and LiAsF$_6$ were ground together in an inert atmosphere glovebox at liquid N$_2$ temperature, sealed in a capillary tube, heated, and annealed. The sample was characterized by powder X-ray diffraction. Details on the preparation method and the experimental instrumentation can be found in ref 28.

After being shipped in a sealed vial, the P(EO)$_6$:LiAsF$_6$ sample was transferred directly to a dry N$_2$ glovebox (VAC Corp., $\leq$1 ppm moisture). Raman and mid-infrared spectra were recorded on the as-received sample. Infrared spectra were recorded with a Bruker IFS66V FT-IR spectrometer over a range of 4000−400 cm^{-1} with a resolution of 1 cm^{-1}. Mid-infrared spectra were taken as KBr pellets. Raman scattering spectra were recorded on an I.S.A. Jobin-Yvon T6400 in the triple subtractive mode with a scan time of 16 s and 10 accumulations using a 180° geometry. The 514 nm line of an argon laser focused through an 80× microscope lens was used for excitation. The laser was operated at 300 mW, and the power at the sample was 50−100 mW. Local heating of the sample by the focused beam was not observed in similar systems.[27]

3. Results and Discussion

A. Symmetry-Based Vibrational Analysis. The isolated AsF$_6^-$ anion has octahedral symmetry, and the symmetries of the six normal vibrational modes are described by the irreducible representations of the O_h

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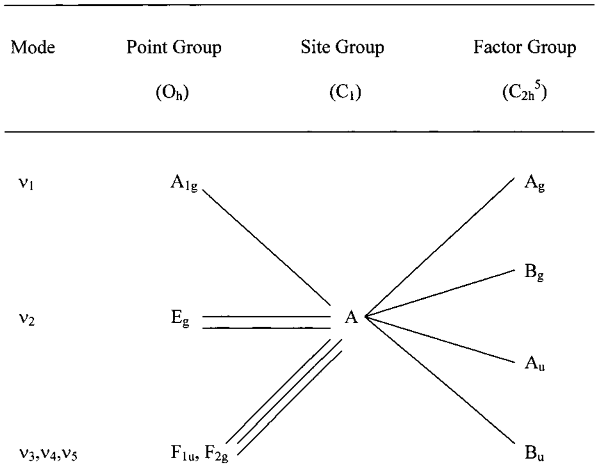
Table 1. Factor Group Correlation of Intramolecular AsF_6^- Vibrations in a C_{2h}^5 Crystal



point group according to

$$\Gamma(\mathrm{AsF_6^-}) = \mathrm{A_{1g} + E_g + 2F_{1u} + F_{2g} + F_{2u}} \qquad (1)$$

The fundamental vibrations, mode labels, and spectral activities of the AsF_6^- ion based on an octahedral geometry have been reported.[29] The crystalline compound $P(EO)_6{:}LiAsF_6$ belongs to the $P2_1/a$ space group,[28] with four AsF_6^- anions in the unit cell. Within the crystal the vibrations of the AsF_6^- anions are not isolated from each other but are correlated through intermolecular forces. The factor group method provides a description of the correlated molecular vibrations as they transform according to the irreducible representations of the factor group.[30] We have previously applied this method to interpret the triflate anion modes in the crystalline compounds $P(EO)_3{:}LiCF_3SO_3$ and P(EO): $NaCF_3SO_3$.[27] In the $P(EO)_6{:}LiAsF_6$ compound the As atoms occupy general 4e positions,[31] and accordingly the site symmetry of the AsF_6^- anions is C_1. The relations between the irreducible representations of the isolated anion, its site group, and the correlated vibrations of the full unit cell are calculated by standard methods[30] and are summarized in Table 1. In this paper we will consider only modes originating in the isolated ion A_{1g} and F_{1u} modes. Table 1 shows that these isolated ion vibrations result in the following factor group modes:

$$\Gamma(\mathrm{A_{1g}}) = \mathrm{A_g + B_g + A_u + B_u} \qquad (2)$$

$$\Gamma(\mathrm{F_{1u}}) = \mathrm{3A_g + 3B_g + 3A_u + 3B_u} \qquad (3)$$

B. Vibrational Modes of the AsF_6^- Anion. The Raman-active $\nu_1(A_{1g})$ mode has been used to determine the presence of ionic association of the AsF_6^- anion in a number of solvents. In solutions of $LiAsF_6$ in 1,2-dimethoxyethane,[32,33] methyl acetate,[34] acetone,[35] water,[34] and tetrahydrofuran,[36] a band occurs in the range of 676−682 cm^{-1} and is assigned to a "spectroscopically free" anion. A "spectroscopically free" anion is indistinguishable from a solvent-separated ion pair by vibrational spectroscopic measurements. In crystalline $CsAsF_6$ the ν_1 mode is observed at 685 cm^{-1}.[29] Systems of $LiAsF_6$−acetone and $LiAsF_6$−methyl acetate display an additional band at 694 cm^{-1} which is assigned to a contact ion pair.[34,35] The intensity of the 694 cm^{-1} band relative to the 676 cm^{-1} band increases with increasing salt concentration. Further support for the contact ion pair assignment is provided by the decrease of the relative intensity of the 694 cm^{-1} band with the addition of 18-crown-6.[34] The crown ether is assumed to coordinate with the Li^+ ion, thereby decreasing the AsF_6^- - -Li^+ contact ion pair formation.

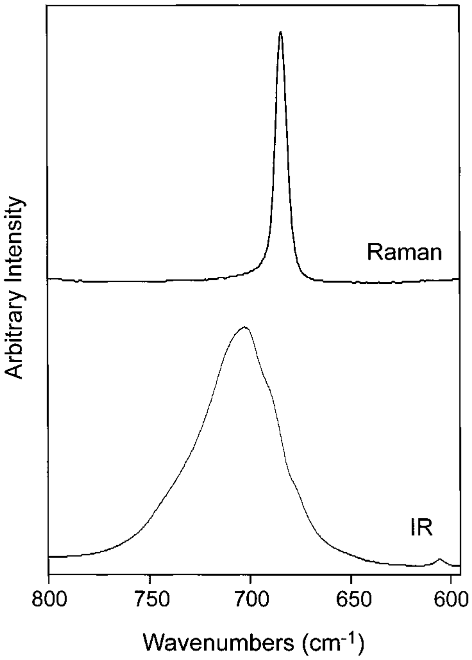


Figure 1. Raman and infrared spectra of the $P(EO)_6{:}LiAsF_6$ compound in the 600−800 cm^{-1} region.

The Raman spectrum of the crystalline complex $P(EO)_6{:}LiAsF_6$ is presented in Figure 1. A single, reasonably symmetrical band is observed at 684 cm^{-1} and assigned to the $\nu_1(A_{1g})$ mode. The absence of a 694 cm^{-1} (or higher frequency) band indicates that no contact ion pairs are present, and the anion exists as a "free" AsF_6^- ion in the crystal. The slightly higher frequency compared to the solvent systems may be a result of crystal packing effects. The symmetry-based vibrational analysis predicts Raman-active bands of A_g and B_g symmetry for this mode in the crystal (eq 2). The degree of factor group splitting of the two components is negligibly small, based on the observation of only a single band.

The infrared-active $\nu_3(F_{1u})$ band has also been used to determine ionic association in AsF_6^- systems. Solutions of $LiAsF_6$ in 2-methyltetrahydrofuan,[37] 1,3-dioxolane,[38] and methyl acetate[39] displayed bands which were assigned to free ions and contact ion pairs at ~702 and ~717 cm^{-1}, respectively. In the IR spectra of the $LiAsF_6$ solutions the intensity of the contact ion pair band is comparable to that of the free ion band, and the area of each band can be resolved by curve fitting. We note that in the $LiAsF_6$−methyl acetate system, where both the Raman and IR spectra were recorded at similar salt concentrations, the contact ion pair band intensity in the IR (717 cm^{-1}) is comparable to the free ion band intensity (702 cm^{-1}).[39] However, in the Raman spectrum the contact ion pair band intensity (696 cm^{-1}) is very weak compared to the free ion band intensity (676 cm^{-1}).[34] Therefore, the bands in the IR are more sensitive to ionic association. In this region an additional band at ~676 cm^{-1} is observed in the solvent systems which has been assigned to a $(\nu_5 + \nu_6)$ combination band ($F_{2g} \times F_{2u} = A_{1u} + E_u + F_{1u} + F_{2u}$).[37] Because this band occurs at the same frequency as the Raman-

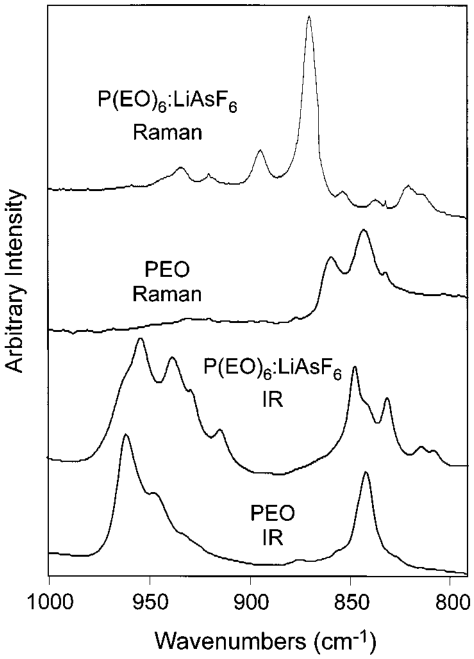


Figure 2. Raman spectra of the P(EO)$_6$:LiAsF$_6$ compound, Raman spectra of the pure PEO, infrared spectra of the P(EO)$_6$:LiAsF$_6$ compound, and infrared spectra of pure PEO in the 800−1000 cm^{-1} region.

active ν_1 mode, it is also possible that the 676 cm^{-1} IR band is due to the ν_1 mode becoming weakly IR-active upon relaxation of the isolated anion O_h symmetry due to solvent−anion interactions.

The infrared spectrum in the region from 640 to 760 cm^{-1}, presented in Figure 1, shows a broad band centered at approximately 702 cm^{-1} with shoulders on the low-frequency side. The analysis of this region is complicated by the fact that both the ν_1 and the ν_3 vibrations have infrared-active components in this area. For the ν_3 vibrations of four coupled AsF$_6^-$ anions in the unit cell, the symmetry-based analysis predicts six IR-active modes, 3A$_u$ + 3B$_u$ (eq 3). Additionally, the ν_1 vibrations are formally predicted to be infrared-active with an A$_u$ and a B$_u$ mode. The major component of the band is at 702 cm^{-1} and is attributed to the ν_3 mode of a free AsF$_6^-$ anion. The broad band shape is attributed to factor group splitting of the ν_3 mode, as stated above. Further evidence for splitting is present in the ν_4 mode (not shown), where multiple band components are observed. Similar splitting patterns are observed in the ν_3 and ν_4 modes in rhombohedral KAsF$_6$.[40] Additional contributions to the low-frequency band structure are the (ν_5 + ν_6) combination band and weakly IR-active components of the ν_1 mode. Because of the broad, complex nature of the band, we cannot completely neglect the possibility that a small contribution from contact ion pairs exists. Such a contribution would presumably originate in the presence of a minor amorphous phase. There is no evidence in the Raman spectrum for such a phase, although the Raman spectrum is less sensitive to the presence of a Li$^+$- -AsF$_6^-$ ion pair than is the IR spectrum.

C. Chain Conformation and CH$_2$ Rocking Modes. In Figure 2 the infrared and Raman spectra of the P(EO)$_6$:LiAsF$_6$ compound are compared with the spectra of pure PEO for the region from 800 to 1000 cm^{-1}. Modes in this spectral region have been assigned to a mixture of predominantly CH$_2$ rocking and C−O stretching motions.[41] The frequencies and intensities of these modes are sensitive to the values of the backbone torsional angles;[15,42,43] thus, the frequency shifts that occur upon complexation with a cation provide insight into the local conformational changes accompanying the polymer−cation interaction.

The conformation of the polymer backbone in P(EO)$_6$:LiAsF$_6$ is significantly different than in crystalline PEO. The conformation of crystalline PEO is (tgt)$_7$ for the dihedral angles C−O−C−C, O−C−C−O, and C−C−O−C, where t is trans and g is gauche.[44] In comparison, the conformation for the same bond sequence in the P(EO)$_6$:LiAsF$_6$ compound is tct-gg′t-gcg′-tct-tgt-g′cg where c refers to cis and g′ refers to gauche-minus.[28]

Both the infrared and Raman spectra of P(EO)$_6$LiAsF$_6$ in this region are more complex than the analogous PEO spectra, with at least five distinct, noncoincident bands visible in each spectrum. In the absence of either a detailed normal coordinate analysis or polarized spectroscopic measurements of an oriented single crystal, it is difficult to make precise vibrational assignments. However, the lack of coincidence in mode frequencies between the Raman and the infrared spectra is clearly due to the presence of a center of symmetry in the unit cell. More specifically, the two polymer chains that comprise a cylindrical structure enclosing the lithium ions also enclose the center of symmetry. Thus, the vibrations of a pair of such chains are correlated through the center of symmetry.

General correlations between torsional angle sequences and frequencies have been previously described. Ethylene oxide units with gauche O−C−C−O torsional angles are reported to have bands in the range 825−890 cm^{-1}, while units with trans O−C−C−O torsional angles exhibit bands in the range 810−825 cm^{-1}.[42,45] The spectra of the P(EO)$_6$:LiAsF$_6$ compound (Figure 2) show a dominant Raman-active band at 871 cm^{-1} and IR-active bands at 848 and 832 cm^{-1}. The crystal structure has two ethylene oxide units with gauche O−C−C−O torsional angles, so the presence of these bands is consistent with the reported structure. In the 810−825 cm^{-1} range, bands are present in both the Raman and infrared spectra of the compound. According to the crystal structure, there are four cis O−C−C−O torsional angles and no trans O−C−C−O torsional angles. Therefore, the bands in the spectral region previously attributed to ethylene oxide units with trans O−C−C−O torsional angles may actually arise from torsional angle sequences rather than a particular value of a torsional angle present in the crystal. Conformation-frequency correlations for the range 900−1000 cm^{-1} are limited because specific torsional angle sequences have overlapping frequency ranges.[42]

4. Conclusions

The vibrational correlation analysis establishes the number and spectral activities of the Brillouin zone center modes originating in the intermolecular vibrations of the AsF$_6^-$ ion. The single band observed in the Raman spectral region of the As−F symmetric stretching mode at 684 cm^{-1} is assigned to the ν_1(A$_{1g}$) mode. The frequency of this band shows that there is no contact ion pairing of the AsF$_6^-$ with the Li$^+$ ion, a result that is consistent with the reported crystal structure. We attribute the broad-band structure of the infrared feature centered at 702 cm^{-1} to the factor group splitting of the ν_3 mode.

Our study of the polymer modes in P(EO)$_6$:LiAsF$_6$ provides insight into the correlation between vibrational frequencies and specific conformational sequences. The CH$_2$ rocking region has a complicated multiplet structure in both the infrared and Raman spectrum. Bands were observed at relatively low frequencies in this region; similar band frequencies in related ethylene oxide-based systems have been previously assigned to ethylene oxide units with trans O−C−C−O torsional angles. However, the clear absence of trans O−C−C−O torsional angles in the crystal structure suggests that these modes may instead originate in the complex torsional angle sequences observed in this compound.

The P(EO)$_6$:LiAsF$_6$ compound represents an interesting structure in polymer electrolytes in that the cation is completely coordinated by the polymer ether oxygens with no coordination by the anion. It has been reported that for LiAsF$_6$ in cross-linked PEO (MW 2000) the AsF$_6^-$ anions exist predominately as free ions even at high salt concentrations.[46] This suggests that the local structure in the low molecular weight, cross-linked PEO may be similar to that in the high molecular weight P(EO)$_6$:LiAsF$_6$ compound.

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