Spectroscopic Studies for Molecular Structure and Complexation of Silver Polymer Electrolytes

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ABSTRACT: Polymer electrolytes containing silver ions have the potential to facilitate transport in membranes for separating olefin/paraffin mixtures. In the present study, the formation of $AgBF_4$ and $AgCF_3SO_3$ complexes with poly(2-ethyl-2-oxazoline) (POZ) and poly(*N*-vinylpyrrolidone) (PVP) was investigated by spectroscopic methods. The carbonyl absorption bands of the infrared and Raman spectra of POZ and PVP with the silver salts confirm complex formation between silver ions and carbonyl oxygens. The symmetric stretching modes for SO_3 of $AgCF_3SO_3$ complexed with PVP were analyzed in terms of "free" anions, ion pairs, and higher-order ion aggregates. The results suggest that the coordination number of silver ion with carbonyl oxygen of POZ and PVP is close to unity, demonstrating unusually high solubility of silver ions in the POZ and PVP matrices. Above the solubility limit, the ion pair and higher-order ion aggregates start to form.

Introduction

Polymer electrolytes have been extensively investigated since reasonably high ionic conductivity was obtained in polyethers, such as poly(ethylene oxide) (PEO) and poly(propylene oxide) (PPO), complexed with alkali metal salts.[1] Most studies have focused on understanding the ionic conductivity, ionic dissociation/association, and morphology in polymer electrolytes, for applications to solid-state batteries, fuel cells, electrochromic displays, etc.[2−5] Polymer electrolytes containing silver ions are of particular interest because of their potential application to facilitated transport membranes for separating unsaturated hydrocarbons from a gas stream.[6−9]

Physical properties of polymer electrolytes strongly depend on the dissociation and association behavior of salts in polymer solvent. Therefore, it is very important to characterize the ionic constituents in polymer electrolytes. Raman and IR spectroscopic measurements have demonstrated the presence of free ions, contact ion pairs, and higher ion aggregates in a number of polymer electrolytes.[10−15] X-ray diffraction, extended X-ray absorption fine structure (EXAFS), and X-ray absorption near edge structure (XANES) in PPO- and PEO-based systems also confirm ionic specification and interactions between anions and cations. [16−18] Schantz et al.[2] carried out a study on poly(propylene glycol) (PPG) complexed with $NaCF_3SO_3$ in the range of O:M = 30:1−5:1 (oxygen to metal concentrations) with Raman scattering measurements. The internal vibrations of anions such as trifluoromethanesulfonate (triflate), $CF_3SO_3^-$, show a clear distinction between free ions, contact ion pairs, and other ion clusters.[2,19,20] In the symmetric $\nu_s(SO_3)$ stretching region, multiple bands have been observed in both IR and Raman spectra. Since the $\nu_s(SO_3)$ mode is nondegenerate, the multiple bands in this spectral region must be associated with the triflate anions in different environments, i.e., free ions, ion pairs, and higher ionic aggregates. In the case of the PPO:$LiCF_3SO_3$ system, the absorption band near 1032 cm^{-1} was attributed to free anionic vibrations, the band near 1042 cm^{-1} to ion pair formation, and the band near 1052 cm^{-1} to vibrations of anions in higher-order ionic aggregates.[14,19,20] The position of bands due to free anions is nearly invariable regardless of the type of cation, whereas band positions due to ion pairs and ion aggregates shift slightly with varying cations. According to the Raman spectra of PPO:$NaCF_3SO_3$ and PPO:$LiCF_3SO_3$ systems,[19] the change to a smaller cation of equal size (from Na^+ to Li^+) results in an increased frequency shift of the higher frequency component (from 1037 cm^{-1} for Na^+ to 1042 cm^{-1} for Li^+), whereas the lower frequency component for the free ion remains invariable at 1032 cm^{-1}.

Investigations have been conducted mostly for alkali metal electrolytes,[2,21] but little is known about the ion dissociation and association in silver electrolyte systems. Raman and IR spectroscopies are employed here to investigate the interactions of silver ions with matrix polymers and characterize the ionic species in poly(2-ethyl-2-oxazoline) (POZ) and poly(*N*-vinylpyrrolidone) (PVP) complexed with $AgBF_4$ and $AgCF_3SO_3$ at various concentrations. Particular attention is focused on those regions of the spectra that display differences upon complexation of silver cation with carbonyl groups of the polymers to provide insight into structural changes and complex formation.

Experimental Section

Poly(2-ethyl-2-oxazoline) (POZ) ($M_w \cong 500\,000$) from Aldrich and poly(*N*-vinylpyrrolidone) (PVP) ($M_w \cong 1\,000\,000$) from Polyscience were used. The silver salts of $AgBF_4$ and $AgCF_3SO_3$ were obtained from Aldrich. All chemicals were used as received. The desired quantities of a polymer and a salt were dissolved in distilled water. The solution was then cast on a glass plate and dried under a N_2 environment. The films were finally dried overnight in a vacuum at room temperature. IR measurements were performed on a Mattson Galaxy 6030 spectrometer; 64−200 scans were signal-averaged at a resolution 4 cm^{-1}. FT-Raman spectra were recorded at room temperature with a Bruker RFS/100S. This experimental setup includes an neodymium-doped yttrium aluminum garnet

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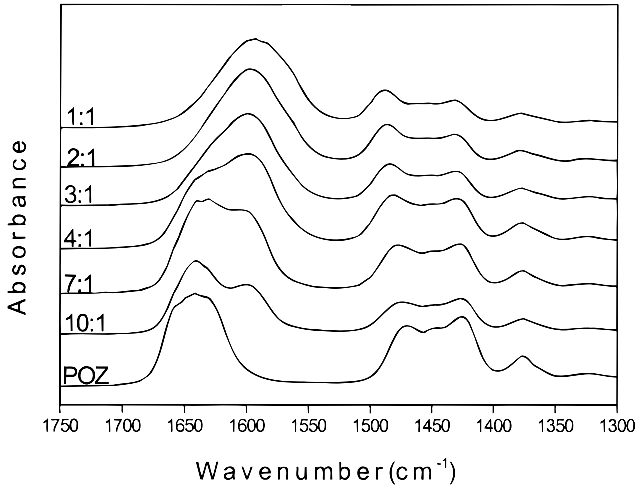

Figure 1. FTIR spectra of pure POZ and the 10:1, 7:1, 4:1, 3:1, 2:1, and 1:1 POZ:$AgBF_4$ complexes over the region between 1750 and 1300 cm^{-1}.

(Nd^{3+}:YAG) laser operating at 1.064 μm with liquid N_2 cooled germanium detector.

Results and Discussion

Figure 1 presents the IR spectra in the carbonyl stretching region for pure POZ and POZ:$AgBF_4$ complexes with various mole ratios of C=O: Ag (e.g., 1:1, 2:1, 3:1, 4:1, 7:1, 10:1). The intensity of the "free" carbonyl stretching band of uncomplexed pure POZ at 1641 cm^{-1} decreased with increasing $AgBF_4$ concentration and disappeared at silver concentrations above 2:1 POZ:$AgBF_4$. A new band at 1595 cm^{-1} appeared upon addition of $AgBF_4$, and its intensity grew with increasing concentration of $AgBF_4$. This new band may be attributable to coordination between the silver ion and carbonyl oxygen. The bands in Figure 1 were deconvoluted into the free C=O band (1641 cm^{-1}) and complexed C=O stretching band (1595 cm^{-1}) as shown in Figure 2. The uncomplexed carbonyl band is evident up to 2:1 POZ:$AgBF_4$ but disappeared completely at the 1:1 POZ:$AgBF_4$ complex. Thus, the 1:1 POZ:$AgBF_4$ complex has only one carbonyl band. This strongly suggests that for a range of C=O:Ag up to a maximum mole ratio of 1:1 there exists a simple coordination interaction of carbonyl oxygen with silver cation.

Figure 3 compares the IR spectrum of pure POZ with the spectra of POZ:$AgCF_3SO_3$ complexes. The vibrational spectra of POZ:$AgCF_3SO_3$ in the C=O stretching region are almost identical to those of POZ:$AgBF_4$ complexes except for a small difference in the band position resulting from complexation.

PVP contains pendant carbonyl groups similar to those of POZ. FT-Raman spectra of pure PVP and PVP:$AgCF_3SO_3$ complexes with mole ratios from 16:1 to 1:1 are shown in Figure 4. The uncomplexed "free" carbonyl stretching band at 1670 cm^{-1} shifts to the lower frequency, and its intensity decreases upon complexation with silver ions. Little difference between 1:1 and 1:2 PVP:$AgCF_3SO_3$ polymer−salt complexes was observed.

These results suggested that $AgBF_4$ and $AgCF_3SO_3$ are dissociated in the polymer solvents (POZ and PVP) due to the coordination interaction of silver ions with carbonyl oxygens, and the silver cation of $AgBF_4$ or $AgCF_3SO_3$ binds to one carbonyl oxygen of POZ or PVP.

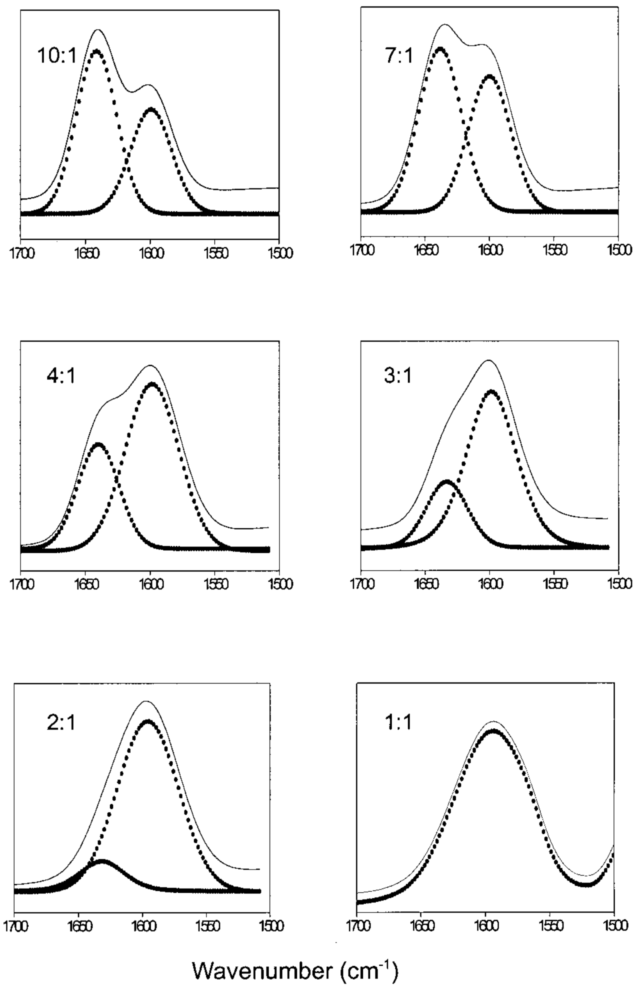

Figure 2. Deconvoluted carbonyl stretching modes for POZ:$AgBF_4$ complexes with varying salt concentrations from Figure 1. Filled circles are for the "free" C=O stretching, and open circles are for the complexed C=O stretching.

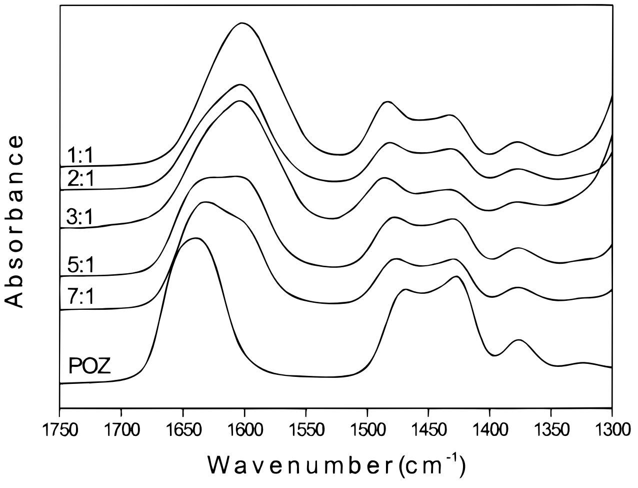

Figure 3. FTIR spectra of pure POZ and the 7:1, 5:1, 3:1, 2:1, and 1:1 POZ:$AgCF_3SO_3$ complexes over the range between 1750 and 1300 cm^{-1}.

It is known that the symmetric SO_3 Raman stretching mode varies among free ions, ion pairs, and higher ionic aggregates,[2,19,20] providing quantitative information on the dissociation and association behavior of salts. The Raman spectra of the ν_1 symmetric stretch of SO_3^- for the triflate in PVP:$AgCF_3SO_3$ in mole ratios from 30:1 to 1:2 (C=O:Ag) are shown in Figure 5. From 30:1 to

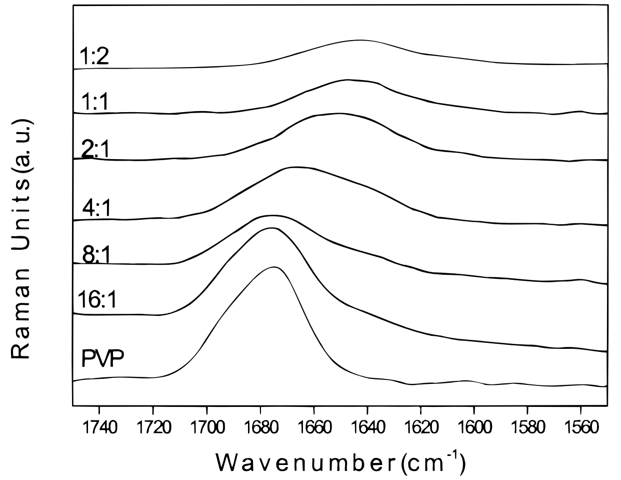

Figure 4. FT-Raman spectra of pure PVP and the PVP:AgCFSO$_3$ complexes with varying salt concentrations.

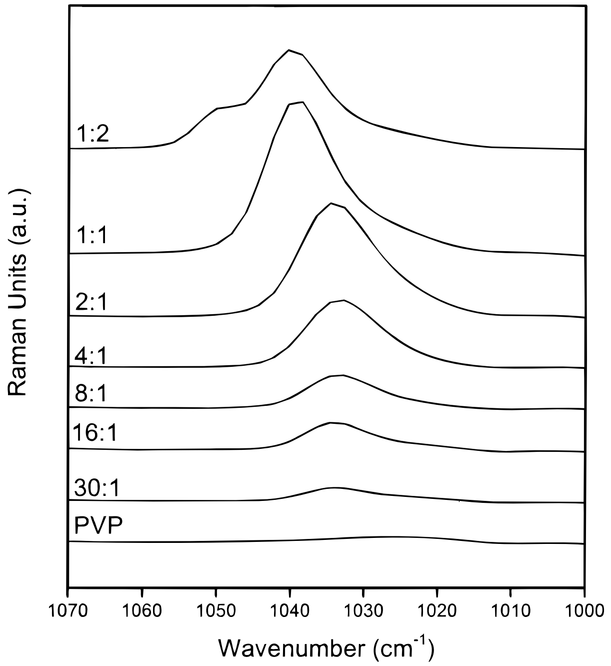

Figure 5. FT-Raman spectra for SO$_3^-$ stretching region of pure PVP and the PVP:AgCF$_3$SO$_3$ complexes.

2:1 PVP:AgCF$_3$SO$_3$, a single band at 1032 cm^{-1} was observed which is associated with the presence of the free anion.[19] When the silver concentration is increased to 1:1, the main band shifts to the higher frequency and the band becomes asymmetric. The asymmetric shape of the band may be attributed to the existence of both free anions and ion pairs. When the silver concentration was raised to 1:2 PVP:AgCF$_3$SO$_3$, the spectrum of the complex has three anion vibrations: a free anion vibration at 1032 cm^{-1} , an ion pair vibration at 1038 cm^{-1}, and higher-order aggregates at 1048 cm^{-1}. The deconvoluted bands of 1:1 and 1:2 PVP:AgCF$_3$SO$_3$ complexes are shown in Figure 6, where a band appears at 1038 cm^{-1} for the 1:1 PVP:AgCF$_3$SO$_3$, demonstrating the existence of ion pairs. The 1:2 PVP:AgCF$_3$SO$_3$ complex shows the presence of higher-order ion aggregates in addition to free ions and ion pairs. This work for AgBF$_4$ and AgCF$_3$SO$_3$ salts complexed with POZ and PVP indicates 1:1 coordination of silver ion by the carbonyl oxygens of POZ and PVP and also the presence of a very fine suspension of solid AgCF$_3$SO$_3$ in the polymer solvents at silver ion concentrations above 1:1 relative to carbonyl oxygen.

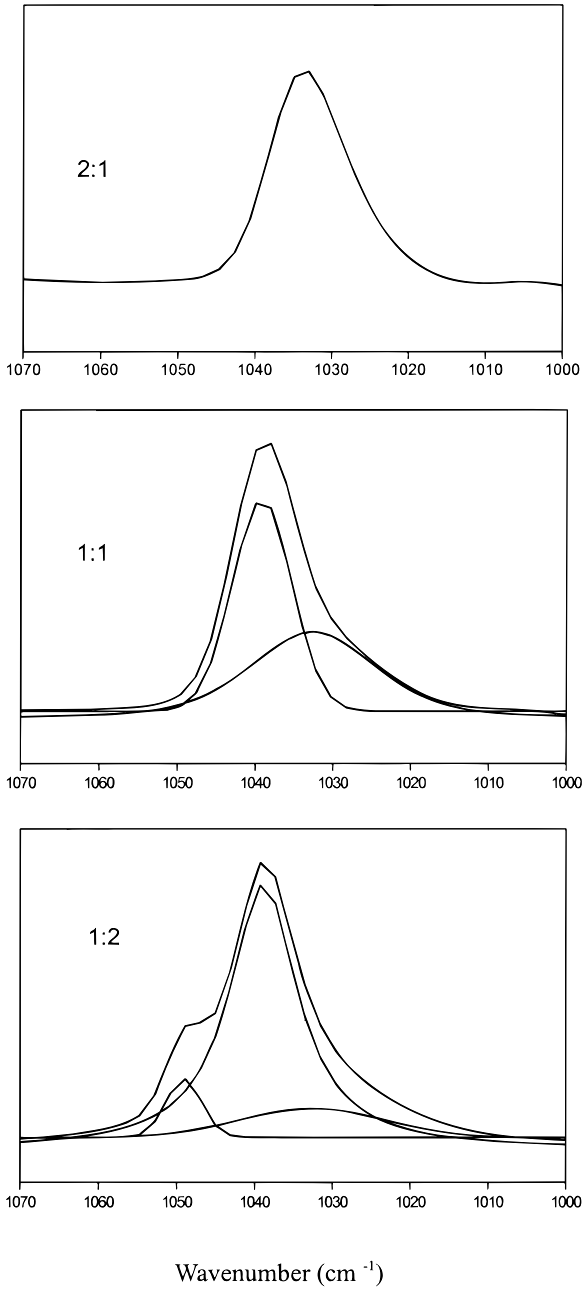

Figure 6. Deconvoluted curves of SO$_3^-$ stretching region for 2:1, 1:1, and 1:2 PVP:AgCF$_3$SO$_3$ complexes from Figure 5.

Conclusion

Silver salts of AgBF$_4$ and AgCF$_3$SO$_3$ are dissolved in polymer solvents POZ and PVP due to the coordination interaction of silver ions and carbonyl oxygens. The ionic constituents of the salts in silver polymer electrolytes were also characterized spectroscopically. The silver cation coordinatively binds to one carbonyl oxygen of POZ or PVP. At silver concentrations above 1:1 relative to carbonyl oxygen, ion pairs start to form, followed by higher-order ionic aggregates.

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